PB84-128685

# Pilot Plant Project for Removing Organic Substances from Drinking Water

Dade County Dept. of Public Health, Miami, FL

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Jan 84

U.S. Department of Commerce
National Technical Information Service

PB84-128685

EPA-600/2-84-009

January 1984

# PILOT PLANT PROJECT FOR REMOVING ORGANIC SUBSTANCES FROM DRINKING WATER

Paul R. Wood, Frances Z. Parsons
Russell F. Lang, Iris L. Payan
Susan S. Espinet-Tracey, Hunt J. Harween
Drinking Water Research Center
Florida International University
Miami, Florida 33199

Doris H. Waddell, Richard A. Coates
Raymond D. Diaz, Martha S. Goldlberg
Miami-Dade Water and Sewer Authority
Hialeah, Florida 33010

Fred W. Curtis, Jr.
Dade County Department of Public Health
Miami, Florida 33125

Cooperative Agreement CR 806890-01

Project Officer

Jack DeMarco
Drinking Water Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

## TECHNICAL REPORT DATA

*(Please read Instructions on the reverse before completing)*

1. REPORT NO.
EPA-600/2-84-009

2.

3. RECIPIENT'S ACCESSION NO.
PB84 128685

4. TITLE AND SUBTITLE
PILOT PLANT PROJECT FOR REMOVING ORGANIC SUBSTANCES FROM DRINKING WATER

5. REPORT DATE
January 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Paul R. Wood, et al.

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Dade County Department of Public Health
1350 N.W. 14th Street
Miami, FL 33125

10. PROGRAM ELEMENT NO.
BNC1A

11. CONTRACT/GRANT NO.
CR806890

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Lab.-Cin.,OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
Project: 12/78 - 12/81

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
Contact: J. Keith Carswell (513)684-7228

16. ABSTRACT

This report describes research on the European practice of preozonation of water to modify naturally occurring organics, followed by bacteria activated carbon (BAC) adsorption to remove trihalomethane precursors. A 100-gal/min pilot plant was designed, constructed and operated to evaluate this process on groundwater in Miami, FL. The raw groundwater feed is representative of sources that are heavily loaded with naturally occurring organics and some volatile chlorinated organics. The first pilot plant study evaluated removal of THMFP by ozone-anaerobic BAC vs. a control system fed nonozonated water.. In the second pilot plant study the ozone and nonozone BAC adsorbers were oxygenated from initial start-up. During both studies, a complete bacterial profile study was conducted to compare with conventional breakpoint chlorination performance. While the pilot plant was being constructed, and during its operation, bench-scale research was also conducted, including: 1) evaluation of GAC adsorptive capacity for THMFP and selected organic pollutants, 2) determination of the source of volatile chlorinated ethene compounds in the local groundwater, and 3) removal of volatile organic pollutants by aeration.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
376

22. PRICE

EPA Form 2220-1 (9-73)

# DISCLAIMER

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under Cooperative Agreement No. CR806890 to the Dade County Department of Public Health. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

# FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

This research project was designed to determine the source of volatile chlorinated organic contaminants in groundwater, develop practical methods of removal in a drinking water treatment plant, and determine the effectiveness of removing trihalomethane precursors in the drinking water treatment plant by a combination of ozonation and bacteria-activated carbon treatment. The purpose of the above was to minimize the level of volatile chlorinated organics in public drinking water supplies.

Francis T. Mayo
Director
Municipal Environmental Research
 Laboratory

# ABSTRACT

A study was conducted to evaluate the European practice of ozonating water to modify naturally occurring organics and then using bacteria-activated carbon (BAC) adsorption to remove trihalomethane (THM) precursors. A 22.7-$m^3$/hr (100-gpm) pilot plant was designed, constructed, and operated to evaluate this process on groundwater in Miami, Florida. The main objective was to extend the bed life of the carbon adsorbers.

Two pilot plant studies were conducted. Pilot Study 1 evaluated removal of THM precursors from ozonated and nonozonated influent treated with anaerobic-bacteria-activated carbon. Later in the study, both BAC adsorbers were oxygenated for aerobic operation to determine whether bed life could be extended by this means. In Pilot Study 2, BAC adsorbers with ozonated and nonozonated influents were oxygenated at initial startup to compare aerobic and anaerobic systems. Throughout all ozone studies, a complete bacterial profile was made for comparison with that of conventional breakpoint chlorination.

Results indicated that ozone applied at about 12 mg/L may be a desirable primary disinfectant for future use in the local south Florida area, but it does not extend bed life enough to make BAC a practical method for removing THM precursors from local groundwater. A cost analysis of the ozone-BAC process was not conducted as part of this project.

In addition to the two pilot studies, bench-scale studies were also conducted to (1) select the best of four commercially available granular activated carbons (GAC's) for use in the pilot plant, (2) determine the ability of GAC to remove agricultural and industrial organic chemicals from waters high in total organic carbon (TOC), and (3) determine the source of volatile chlorinated ethene compounds in raw groundwater in the Miami area and other parts of Florida. Results of the bench studies are presented in the appendices to the main report.

This report was submitted in fulfillment of Cooperative Agreement No. CR806890 by Florida International University and Miami-Dade Water and Sewer Authority under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period October 1, 1978, to December 31, 1982, and work was completed as of December 31, 1982.

## CONTENTS

Foreword . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . iii
Abstract . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . iv
Abbreviations, Symbols, and Metric Equivalents . . . . . . . . . . . . . vi
Acknowledgments . . . . . . . . . . . . . . . . . . . . . . . . . . . . vii

1. Introduction . . . . . . . . . . . . . . . . . . . . . . . . . 1
2. Conclusions . . . . . . . . . . . . . . . . . . . . . . . . . 3
3. Recommendation . . . . . . . . . . . . . . . . . . . . . . . . 6
4. Equipment and Procedures . . . . . . . . . . . . . . . . . . . 7
5. Pilot Plant Study No. 1: Effects of Ozonated Influent on THMFP with an Anaerobic BAC System . . . . . . . . . . . . . . . . . . 13
6. Pilot Plant Study No. 2: Effects of Ozonated Influent on THMFP with an Aerobic BAC System . . . . . . . . . . . . . . . . . . . 60

Appendices

A. Experimental Design 1: Bench-Scale Studies of GAC Types . . . . 149
B. Experimental Design 2: Using Aeration to Remove THMFP . . . . . 253
C. Experimental Design 3: Determining the Source of Volatile Chlorinated Organics in Raw Influent to the Preston Plant . . . 315

References . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 365

# ABBREVIATIONS, SYMBOLS, AND METRIC EQUIVALENTS

## Abbreviations and Symbols

| | |
|---|---|
| GAC | granular activated carbon |
| BAC | bacteria-activated carbon |
| EBCT | empty bed contact time |
| THM | trihalomethane |
| TTHM | total trihalomethane |
| THMFP | trihalomethane formation potential |
| TOC | total organic carbon |
| HOC | halogenated organic compounds |
| ED | experimental design |
| PS 1 | Pilot Plant Study No. 1 |
| PS 2 | Pilot Plant Study No. 2 |

## METRIC EQUIVALENTS

| | | |
|---|---|---|
| gal | gallon | 3.785 liters |
| gpm | gallon per minute | $0.227/m^3/hr$ |
| gpm/ft$^2$ | gallon per minute/square foot | $2.445/m/hr$ |
| MGD | 1 million gallons/day | $157.7\ m^3/hr$ |
| ft. | foot | 0.3048 meter |
| lb | pound | 0.454 kg |

# ACKNOWLEDGMENTS

The most valuable help, leadership, and guidance for the project was provided by the Project Officer, Mr. Jack DeMarco. His effort in designing the research and keeping it moving in the proper direction and time frame was the major reason for its success.

The support and cooperation of Gregory B. Wolfe, President of Florida International University, Mr. Garrett Sloan, Director of the Miami-Dade Water and Sewer Authority, and Dr. Richard Morgan, Director of the Dade County Department of Public Health, are greatly appreciated. Close support was needed and received from Lambert Tall, Dean of the School of Technology, Florida International University.

# SECTION 1

# INTRODUCTION

This project addresses the problem of removing organic substances from drinking water by a European method of ozonating water to modify naturally occurring organics and then using bacteria-activated carbon (BAC) adsorption to remove trihalomethane (THM) precursors. The project resulted from an earlier 3-year study of carbon adsorption showing that at a flow rate of 7.35 m/hr (3 gpm/ft $^2$, 3.05 m (10 ft.) of BAC and an empty-bed contact time (EBCT) of 24.8 minutes were required to achieve a bed life of 81 days (Ref. 1). This bed life was based on the number of days required to reach a certain breakthrough of trihalomethane formation potential (THMFP). The breakthrough was the point at which the total trihalomethanes (TTHM's) reached 100 µg/L when the effluent was rechlorinated to a free chlorine residual of 2.5 mg/L and held for 2 days.

The purpose of the present study was to extend this bed life by using the European method of ozonation and carbon adsorption. This treatment technique took advantage of aerobic biological oxidation on granular activated carbon (GAC). Bed life was said to extend well beyond the period of pure adsorption, and the mechanism appeared to be one by which biodegradable organics were metabolized by bacteria growing on the GAC. Further extension of bed life could reportedly be obtained by ozonation of the water feeding the GAC adsorbers. This ozonation was believed to modify the naturally occurring organics and render them more readily degradable by the bacteria.

Consequently, a 22.7-m$^3$/hr (100-gpm) pilot plant was designed, constructed, and operated to evaluate this process on groundwater in Miami, Florida. The pilot plant was located at the Preston Water Treatment Plant in Hialeah, Florida. The raw groundwater feed was from wells 27.4 m (90 ft.) deep on the plant site and contained substantial amounts of naturally occurring organics—8 to 10 mg/L total organic carbon (TOC) and 600 to 800 µg/L THMFP.

The pilot plant was designed to study parallel systems of GAC adsorbers that were 3.05 m (10 ft.) deep, had an EBCT of 24.8 minutes, and received ozonated and nonozonated, lime-softened water that was recarbonated to pH 8.5 and sand filtered. The GAC adsorbers were operated under anaerobic conditions in the first study and aerobic conditions in the second study. The adsorbed ozone dosages in these studies were 11.3 and 14.5 mg/L, respectively. The bed life for each of the two parallel systems was determined.

In addition to the pilot studies to extend GAC bed life, bench-scale studies were conducted to determine:

1) The best of four commercially available GAC's for removing THM

2) The bacteria profile of the Preston Water Treatment Plant, including the distribution system.

3) The bacteria profile of the bench-scale GAC work.

4) The ability of GAC to remove agricultural and industrial organic chemicals from waters high in TOC.

5) The source of chloroethene compounds present in raw groundwater in the Miami area and in other locations in Florida.

6) Removal of volatile halogenated organics from water by aeration techniques.

These studies are detailed in the appendices to the main report.

## SECTION 2

## CONCLUSIONS

### CHEMICAL PARAMETERS

1. Of the four commercially available GAC's tested for THMFP removal on finished water, Calgon Filtrasorb 400 gave the longest bed life and was selected for the pilot plant study.

2. When a 2.13-m-deep (7-ft.) bed of Filtrasorb 400 was tested for THMFP removal on lime-softened, sand-filtered water adjusted to a pH of 8.5, the Criterion 1 bed life[*] was 21 days.

3. In the first pilot plant study, the ozone- and nonozone-GAC systems were operated anaerobically for the first 98 days of the 160-day test. Based on Criterion 1, the bed life was 44 days for the ozone-GAC system and 19 days for the nonozone control system.

4. In the first pilot study, changing from anaerobic to aerobic operation did not appear to alter the shape of the pseudo-steady-state portion of the TOC or THMFP breakthrough curves.

5. In the second pilot plant study, the ozone- and nonozone-GAC systems were operated aerobically throughout the full 172-day test period. Based on Criterion 1, the bed life was 25 days for the ozone-GAC system and 9 days for the nonozone control system.

6. Because the TOC and THMFP loadings were different for the two pilot studies (anaerobic and aerobic), direct comparisons were impractical.

7. Ozone in the ozone contactors greatly reduces the concentration of double-bond chlorinated compounds. At an absorbed ozone dose of 14.5 mg/L, the initial concentration of cis 1,2-dichloroethene, vinyl chloride, and chlorobenzene was reduced 90, 91, and 94 percent, respectively. At an absorbed ozone dose of 4.25 mg/L, these compounds were reduced 73, 88, and 78 percent, respectively.

8. In a 335-day test of the removal of spiked organics from finished water, several polyaromatic hydrocarbons (PAH's), several halogenated pesticides, and one polychlorinated biphenyl (PCB) were fed to a 0.76-m-deep (2.5-ft.) bed of Filtrasorb 400. During the test period, this GAC removed essentially 100 percent of all the PAH's, 98.6 percent of all the halogenated pesticides, and 97.5 percent of the PCB.

---

[*] When 3 mg/L of TOC or 200 μg/L of THMFP breakthrough occurs, subsequent chlorination to 2.5 ppm of free chlorine (1 hour of chlorine contact time) results in a THM growth of 100 μg/L (after aging 2 days or until all free chlorine is gone).

9. In an aeration system (i.e., stirred beaker, aeration tower, spray head), the decrease in contaminant levels in water over time is linear if the log of the effluent concentration is plotted versus time and if all compounds present are in the soluble range.

10. When aeration decreases contaminant levels in water over time, the decrease is independent of other organic compounds when all compounds are present in the soluble state. The decreased concentration over time is also independent of initial concentration in the range of solubility.

11. The source of volatile chloroethene compounds (vinyl chloride, vinylidene chloride, cis and trans 1,2-dichloroethylene, etc.) in the local groundwater is a result of the biodegradation of parent, volatile, chlorinated degreasing solvents accidentally spilled on the ground above the aquifer. The solvents were trichloroethylene and/or tetrachloroethylene. Chloromethane and ethane compounds are the result of the biodegradation of 1,1,1-trichloroethene.

12. Field data from an actual contaminant spill in the environment confirmed the results of the laboratory biodegradation studies.

## BIOLOGICAL PARAMETERS

1. In the GAC beds used to filter raw, lime-softened, or chlorinated finished drinking water, large numbers of bacteria grew and sloughed off into the water flow.

2. Bacteria isolated from the GAC adsorbers were common to the raw water supply and were normal inhabitants of soil and fresh-water sediments.

3. Often, many of the bacteria that made up the total plate counts (and those most frequently encountered) were unidentifiable by taxonomic keys, did not survive subculturing, or were inert in standard biochemical tests.

4. Common heterotrophic organisms recovered from raw and treated water from the bench-scale tests, the pilot plant, and the full-scale treatment plant were species of Alcaligenes, Pseudomonas, Moraxella, Acinetobacter, Micrococcus, Flavobacterium, and Gram-positive rods.

5. The composition of the GAC effluent flora was generally the same as that of the flora on the GAC surface, but the species existed in different proportions. Perhaps these results reflect different resistances of the species to dislodgement by the water flow.

6. No real differences existed in the numbers or kinds of bacteria recovered from the GAC adsorber effluents that received aerated, oxygenated, ozonated, or untreated influents. Many of the heterotrophic bacteria cultured from samples of the GAC or their effluents were able to grow well without atmospheric oxygen.

7. Bacterial populations in the GAC adsorbers were dynamic. Periodic sampling and analyses indicated that the sizes and compositions of these

populations changed constantly. Probable causes were succession of species within the adsorber and introduction of new species from the raw groundwater supply.

8. Gram-negative rods, which had no especially resistant forms, survived in GAC effluents that were chlorinated to breakpoint and had up to 10 mg/L free residual chlorine at the time of plating.

# SECTION 3

# RECOMMENDATION

Ozone applied in the 12-mg/L range may be a desirable in-plant primary disinfectant for future use in the local south Florida area. At this concentration, ozone appears to be as effective as current breakpoint chlorination at 18 mg/L for pathogen and microorganism control, and it may provide even better color reduction. At this dosage, ozone also effectively oxidizes double-bond chlorinated compounds that are present in the raw groundwater. For residual control in the distribution system, ozone could be followed by a secondary disinfectant that would not form additional THM's.

If the local groundwater source ever becomes contaminated with organic compounds that are not readily removed by other means, the use of GAC adsorption in this high-TOC water would be very effective and should be considered.

# SECTION 4

# EQUIPMENT AND PROCEDURES

## PLANT CONDITIONS

Conclusions in this report are based on the particular groundwater feed and water treatment practices existing at the Preston Water Treatment Plant during the study period. Groundwater containing high concentrations of TOC and THM precursors was lime softened, breakpoint chlorinated, and sand filtered. Finished water leaving the plant had a free chlorine residual of 2.5 to 3.0 mg/L for continued disinfection in the distribution system. The average TTHM concentration in the finished water was 150 µg/L. This concentration increased to 300 µg/L in the distribution system because of the continued reaction of free chlorine residual with precursor substances remaining in the finished water.

Both the original research project and the present study were based on the possibility of removing enough THMFP at the water treatment plant to limit further growth of TTHM in the distribution system to 100 µg/L (assuming that the finished water left the plant with a free chlorine residual of 2.5 to 3.0 mg/L).

Under the given plant conditions, a GAC adsorber effluent breakthrough of approximately 3 mg/L of TOC or 200 µg/L of THMFP was found to produce the 100 µg/L TTHM concentration. In this report, bed life based on these conditions is referred to as "Criterion 1 bed life."

## PROCEDURES

### Pilot Studies

The first of the two pilot plant studies evaluated the effects of ozonated and nonozonated influent on the removal of THMFP with GAC adsorbers operated under anaerobic conditions. After the pseudo-steady-state region of the THMFP breakthrough curve was reached on the GAC adsorber effluents, both GAC adsorbers were oxygenated for aerobic operation to determine whether the effective GAC bed life could be extended by a change to aerobic operation.

In the second pilot plant study, both ozonated and nonozonated GAC systems were oxygenated on initial startup to compare aerobic operation with the anaerobic operation of the first study. Other studies were conducted in the pilot plant to determine how TOC and THMFP were affected by absorbed ozone dosages at various pH ranges.

Throughout all ozone studies, a complete bacterial profile was made to be compared with that of conventional breakpoint chlorination.

## Bench-Scale Studies

Both bench- and pilot-scale studies were conducted at the same time. The first bench-scale project was designed to select the best of four commercially available GAC's for use in the pilot plant. Selection was based on the greatest adsorptive capacity (longest bed life) for removing THM precursors from the Preston plant finished water. The best GAC selected was then evaluated for bed-life performance on lime-softened Preston plant water that was first adjusted to pH 8.5 by recarbonation and then sand filtered. This type of water feed was used to supply both the ozonated systems and the nonozonated controls.

During the bench-scale studies, a complete bacteria profile was made for the Preston plant. This profile included the distribution system and all bench-scale systems.

Methods were developed during the bench-scale studies for continuous spiking of plant effluents with agricultural and industrial pollutants. Studies were then made on the removal of these compounds by the GAC adsorbers. Such information will be useful if the local groundwater supply ever becomes contaminated, since little is known about the ability of GAC to remove such pollutants from high-TOC waters.

Bench-scale studies were also conducted to determine the source of volatile, chlorinated ethene compounds in raw groundwater in the Miami area and in other locations in Florida

## PILOT PLANT DESIGN

A 150,000-gal/day (100 gpm) pilot plant was constructed at the 100-mgd Preston Water Treatment Plant, Hialeah, Florida (part of Greater Miami). More than 4 years of research data have been collected at this site (Refs. 1-6). The pilot plant was designed in three sections. Section I is the water treatment portion of the plant, consisting of conventional lime softening, breakpoint chlorination, and sand filtration. Section II includes the ozone generating and contacting units. Section III houses the BAC, post chlorination, and storage units.

## PILOT PLANT SECTION I

The Section I treatment processes of conventional lime softening, breakpoint chlorination, and sand filtration are diagrammed in Figure 1. In previous research, the raw water feed for the project consisted of a composite raw water feed obtained from seven 90-ft.-deep wells located on the plant site. During this research phase, we attempted to draw the composite raw water feed to the pilot plant mostly from the same on-site wells. But in the meantime, a plant expansion of the Preston plant from 60 to 100 mgd was completed, and water from a new well field further west in the Everglades was blended with the on-site water. Thus the raw water that we received at the pilot plant was variable, depending on the ratio of draw from the new higher TOC well field and a complex set of blending factors in the Preston plant. The raw water averaged 10.6 mg/L of TOC, 586 μg/L THMFP, 25 color units, and a total hardness of 250 mg/L. Activated silica (2 mg/L) was added to the raw water before the lime softener as a flocculation aid. An Accelator Treatment Unit, manufactured by Infilco Degremont, Inc., Richmond, Virginia, was used for lime softening (100 gpm design capacity). The effluent water from the Accelator averaged 9.8 pH, 53 mg/L total hardness, and 14 color units. After the Accelator, 1 mg/L tripolyphosphate (W-139, Mogul Corp., Chagrin Falls, Ohio) was added for calcium carbonate stability and corrosion control. The water was then passed through the recarbonation tank for pH adjustment with carbon dioxide. Recarbonation was not used with breakpoint chlorination, as chlorination alone in the Preston plant was adequate for pH reduction. Recarbonation was followed by breakpoint chlorination (18 mg/L of chlorine). The chlorinated water then proceeded through the three chlorine contact basins, furnishing the 1-hr contact time as practiced in the Preston plant. The water then entered a sand filter (Infilco Degremont) at a flow rate of 3 gpm/ft.$^2$. Finished water was sampled from the clearwell. This arrangement was used to confirm that the pilot plant provided finished water of similar quality to the full-scale Preston plant.

## PILOT PLANT SECTION II

The flow diagram for Section II, the ozone generation and contacting part of the pilot plant, appears in Figure 2. A Kerag Ozonator, manufactured by Howe-Baker, Tyler, Texas, supplied 70 g $O_3$/hr. Water from the clearwell (Figure 1) entered the gravity feed tank (Figure 2). The first ozone contactor was a Kerag Design RB 90/200 Mechanical Ozone Injection System (stainless steel). The rotating mechanical disc in the unit produced a partial vacuum that was used to move the chilled air through the ozonator and transfer it to the rotating disc head. Thus it was essential that the water flow to and from the mechanical contactor was cotrolled by gravity feed. Hereafter in this report, this contactor will be referred to as the mechanical ozone contactor (MOC). At the water flow rate of 25 gpm, the retention time was 2.8 minutes in the MOC, and the average ozone transfer efficiency was 54 percent.

The stainless steel tank following this unit was originally designed to provide additional ozone contact time. To increase the ozone transfer efficiency, this tank was transformed into a bubble ozone contactor (BOC). A stainless steel bellows pump (Metal Bellows Corp., Sharon, Massachusetts) was installed to move the exhaust gas from the MOC through nine stainless steel gas spargers in the stainless steel tank, making it a bubble contactor. To increase the transfer efficiency, ozonated water in the BOC was sprayed through a stainless steel spray head down through a section of the exhaust gas pipe on the BOC.

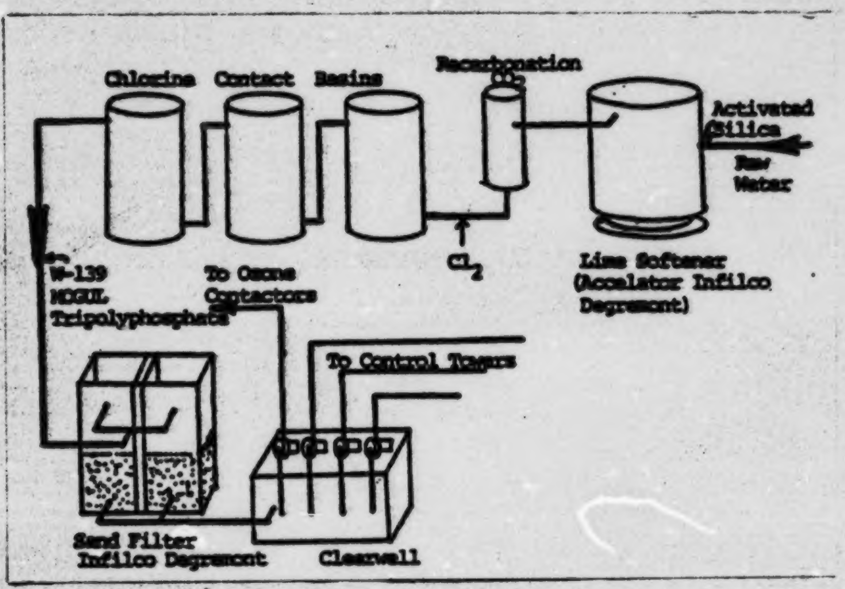

Chlorine Contact Basins
Recarbonation
$CO_2$
Activated Silica
Raw Water
$Cl_2$
Lime Softener
(Accelator Infilco Degremont)
W-139
MOGUL
Tripolyphosphate
To Ozone Contactors
To Control Towers
Sand Filter
Infilco Degremont
Clearwell

Figure 1. Section I of pilot plant: Lime softening, breakpoint chlorination, and sand filtration.

[redacted]

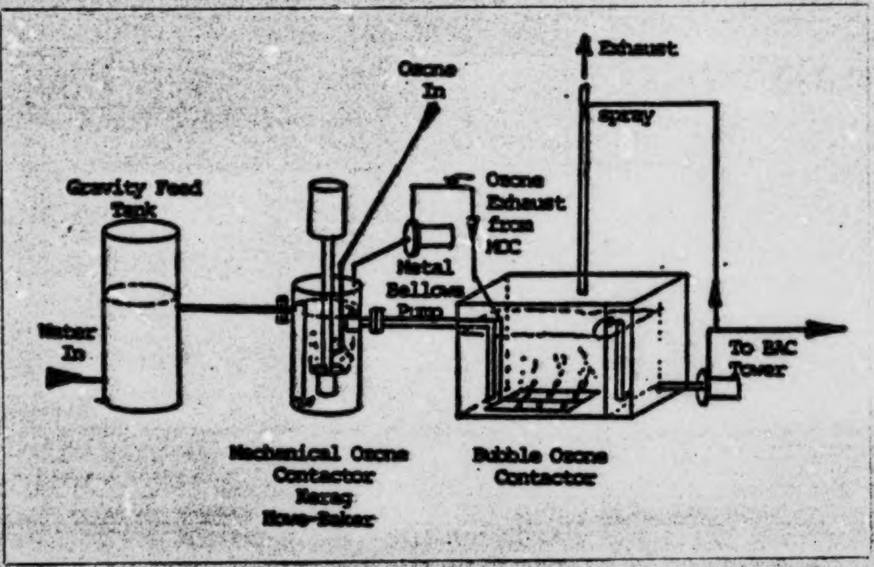

Exhaust
Ozone In
spray
Gravity Feed Tank
Ozone Exhaust from MOC
Metal Bellows Pump
Water In
To BAC Tower
Mechanical Ozone Contactor
Kerag
Hove-Baker
Bubble Ozone Contactor

Figure 2. Section II of pilot plant: Ozone generation and contacting.

## PILOT PLANT SECTION III

The flow diagram for Section III—the bacteria-activated tower (BAT), chlorine contact basin, and storage units—appears in Figure 3. This section of the pilot plant contained four tower sections, only three of which were used in the first research phase (as shown in Figure 3). The BAT's were manufactured by M-B Squared, Pittsburgh, Pennsylvania, and were 38 inches inside diameter, 16 ft. high, and contained 10 ft. of adsorbent, with water sampling ports at 2.5, 5, 7.5, and 10 ft. A sample port for removing solid adsorbent was also provided. The water flow through the towers was 3 gpm/ft.$^2$. BAT Section A (Figure 3) received ozonated water. BAT Sections C and D received nonozonated water. After each tower, the water was chlorinated before entering the chlorine contact basin that followed each tower. The level of chlorination was adjusted to provide a 2.5-ppm free chlorine residual after a contact time of 1 hr. Filtrasorb F-400, a GAC manufactured by Calgon Corp., Pittsburgh, Pennslyvania, was used in this first pilot plant research phase (in Towers A and D) because bench-scale studies showed it to be the best of four commercial carbons for precursor removal (see Appendix A). From the BAT sections, the removal of TOC, THMFP, and specific organic chemicals present in the water at 2.5, 5, and 10 ft. of BAT depth was determined, as well as the THM growth after chlorination, which increased as precursor breakthrough occurred. The three BAT's permitted comparisons of ozonated and nonozonated BAC, and they showed the effects of bacteria in a nonadsorbent sand tower.

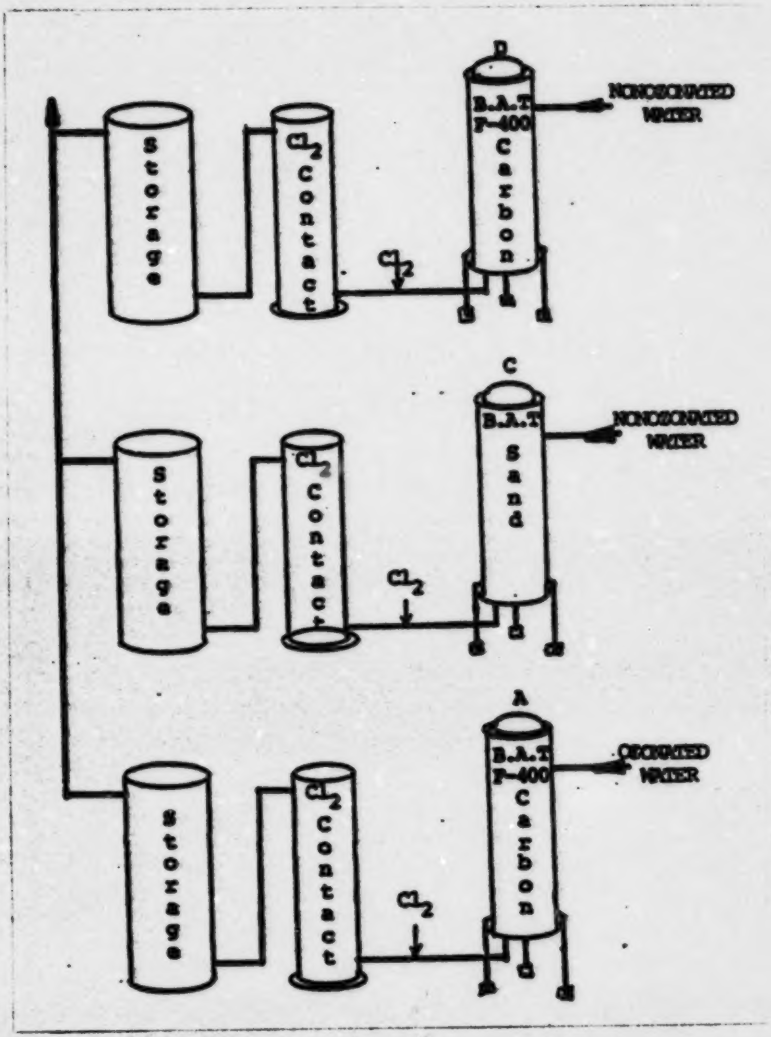

D
B.A.T
F-400
Carbon
NONOZONATED WATER
Storage
Cl2
Contact
Cl2
C
B.A.T
Sand
NONOZONATED WATER
Storage
Cl2
Contact
Cl2
A
B.A.T
F-400
Carbon
OZONATED WATER
Storage
Cl2
Contact
Cl2

Figure 3. Section III of pilot plant: Bacteria-activated towers, chlorine contact basin, and storage.

# SECTION 5

## PILOT PLANT STUDY NO. 1: EFFECTS OF OZONATED INFLUENT ON THMFP WITH AN ANAEROBIC BAC SYSTEM

In our previous research with adsorbents (Ref. 1-6), we developed background data on precursor removal by GAC columns with their associated anaerobic bacteria colonies. This first ozone-BAC work in Pilot Plant Study No. 1 (PS 1) was designed to begin operation of the BAT's without added oxygen, which would result in an anaerobic system. With this approach, a base of data after ozonation would be developed to be compared with our previous adsorbent data base, also under similar anaerobic conditions. In this study, after lime softening, the water was adjusted to a pH of 8.5 with carbon dioxide. No chlorine was added. Water from the clearwell (25 gpm) was pumped individually to the ozone contactors and to the two control BAT's, one sand and one GAC. Water from the contactor was then pumped to the ozone-BAC tower. The effluent from each of the three towers was breakpoint chlorinated, followed by a chlorine contact time of 1 hr before passing into the storage tanks. From raw water to final storage to additional laboratory storage, a complete profile was obtained for wet chemistry, halogenated organics, TOC, THMFP, and bacteria.

When TOC and THMFP breakthrough seemed to reach the plateau portion of the breakthrough curve, oxygen was added to all three towers to determine whether the plateau level, or gradual rate of plateau rise, could be reduced. Results of the first research phase follow. The phase began September 9, 1980, and ended February 27, 1981. Excluding down time, the actual run time was 160.5 days. Complete chemical and biological parameters are discussed for each of the three pilot plant stages here and in Section 6.

### RESULTS FOR CHEMICAL PARAMETERS STUDIED

### Pilot Plant Section I Chemical Data

### Turbidity—NTU

Throughout the test period, the raw water turbidity average was 0.43. After recarbonation and sand filtration, the average value was 0.4 in the clearwell.

### Color—Units of Apparent Color

Lime softening reduced the raw water color from 25 to 14. Breakpoint chlorination reduced clearwell water from a color value of 11 to 3. Ozonation reduced the same water to a value of 2 color units. Thus with our water, ozone was at least as effective as breakpoint chlorination for color reduction. The complete color profile appears in Table 1.

TABLE 1

AVERAGE COLOR PROFILE VALUES FOR FIRST
OZONE-BAC STUDY

| Sample Location | Average Color Units | Remarks | |
|---|---|---|---|
| Raw Water | 25 | Samples of clearwell water were periodically chlorinated to breakpoint. Color averaged 3 | |
| Lime Softener Effluent | 14 | | |
| Clearwell Effluent | 11 | | |
| MOC + BOC Effluent | 2 | | |
| | A-Tower (Ozone-BAC) | C-Tower (Nonozone-sand) | D-Tower (Nonozone-BAC) |
| 2.5 Ft. | 1 | 11 | 5 |
| 5 Ft. | 1 | 11 | 3 |
| 10 Ft. | 1 | 11 | 2 |
| 10 Ft. Effluent | | | |
| Breakpoint Chlorinated | 1 | 6 | 2 |

## pH—

After recarbonation and sand filtration, the pH values for raw water, lime-softened effluent, and clearwell effluent were 7.1, 9.9, and 8.5, respectively.

## Halogenated Organics—

The halogenated organic profile for Section I of the pilot plant is shown in Table 2.

## TABLE 2

## AVERAGE CONCENTRATION (μG/L.) OF HALOGENATED ORGANICS IN PILOT PLANT SECTION 1

| Compound | Raw Water | Lime-Softened Water | Clearwell Water |
|---|---|---|---|
| Vinyl Chloride | 11.0 | 11.0 | 7.4 |
| Methylene Chloride | 0.2 | 0.27 | 0.34 |
| Trans 1,2-Dichloroethene | 0.9 | 0.9 | 0.7 |
| 1,1-Dichloroethane | 2.0 | 2.1 | 1.6 |
| Cis 1,2-Dichloroethene | 24.0 | 23.0 | 22.0 |
| Chloroform | **0.85<br>***ND | **0.88<br>ND | *0.8<br>ND |
| Trichloroethylene | 0.45 | 0.36 | 0.33 |
| Bromodichloromethane | ND | ND | ND |
| Tetrachloroethylene | ND | ND | ND |
| Chlorodibromomethane | ND | ND | ND |
| Chlorobenzene | 0.6 | 0.4 | 0.4 |
| Bromoform | ND | ND | ND |
| p-Chlorotoluene | ND | ND | ND |
| m-Dichlorobenzene | ND | ND | ND |
| p-Dichlorobenzene | 0.2 | 0.1 | 0.06 |
| o-Dichlorobenzene | 0.11 | 0.06 | 0.03 |

* First 21 days
** Through day 24.3, none detected thereafter
*** None detected

Methylene chloride levels were reported for the first 21 days. The level was very low in raw water, averaging 0.2 μg/L. After test day 21, reporting stopped because blanks on the gas chromatograph became high and variable from day to day because of the use of methylene chloride for extraction of pilot plant samples for higher-molecular-weight trace organics.

Low levels of chloroform were found in the raw water through test day 24 because of a slight feedback from the Preston plant lime softener (formed in the coagulation aid by chlorine activation of sodium silicate). This was corrected, and no chloroform was detected for the remainder of the test. Lime-softened water from the pilot plant and the full-scale Preston plant were periodically breakpoint-chlorinated to compare instantaneous THM growth after 1 hr of chlorine contact time with a free chlorine level of 2.5 ppm. Average values of individual and total THM's appear in Table 3.

## TABLE 3

## THM GROWTH IN LIME-SOFTENED, BREAKPOINT-CHLORINATED PILOT- AND FULL-SCALE PLANTS

| Instantaneous THM Growth (µg/L) | | |
|---|---|---|
| | Pilot Plant | Preston Plant |
| Chloroform | 29.1 | 27.5 |
| Bromodichloromethane | 17.3 | 17.7 |
| Chlorodibromomethane | 13.4 | 12.7 |
| Bromoform | 1.9 | 1.4 |
| Total THM's | 61.7 | 59.3 |

The closeness of these values indicate that the pilot plant and full-scale Preston plant performed comparably.

### TOC—

TOC profile data for Section I are graphed in Figure 4. Average TOC values for raw, lime-softened and clearwell water were 10.6, 7.8, and 7.7 mg/L, respectively. Lime softening removed an average of 26 percent, and sand filtration lowered the value to 27 percent. The full-scale Preston plant performance was similar.

### THMFP—

THMFP data are plotted in Figure 5. The average THMFP values in raw, lime-softened and clearwell water were 586, 427 and 438 µg/L, respectively. Lime softening removed 27 percent. Sand filtration essentially did not bring about a further reduction since the two values, 427 and 438 mg/L, are essentially equal. Preston plant performance was similar.

## Pilot Plant Section II Chemical Data

### Absorbed Ozone Dose—

The Kerag RB 90/200 MOC provided an ozone transfer efficiency of 54 percent. Contact time in the MOC was 2.8 minutes. The ozone content of the MOC effluent averaged 0.88 mg/L. When an effluent sample was taken and held 2.2 minutes before ozone analysis, representing a total contact time of 5

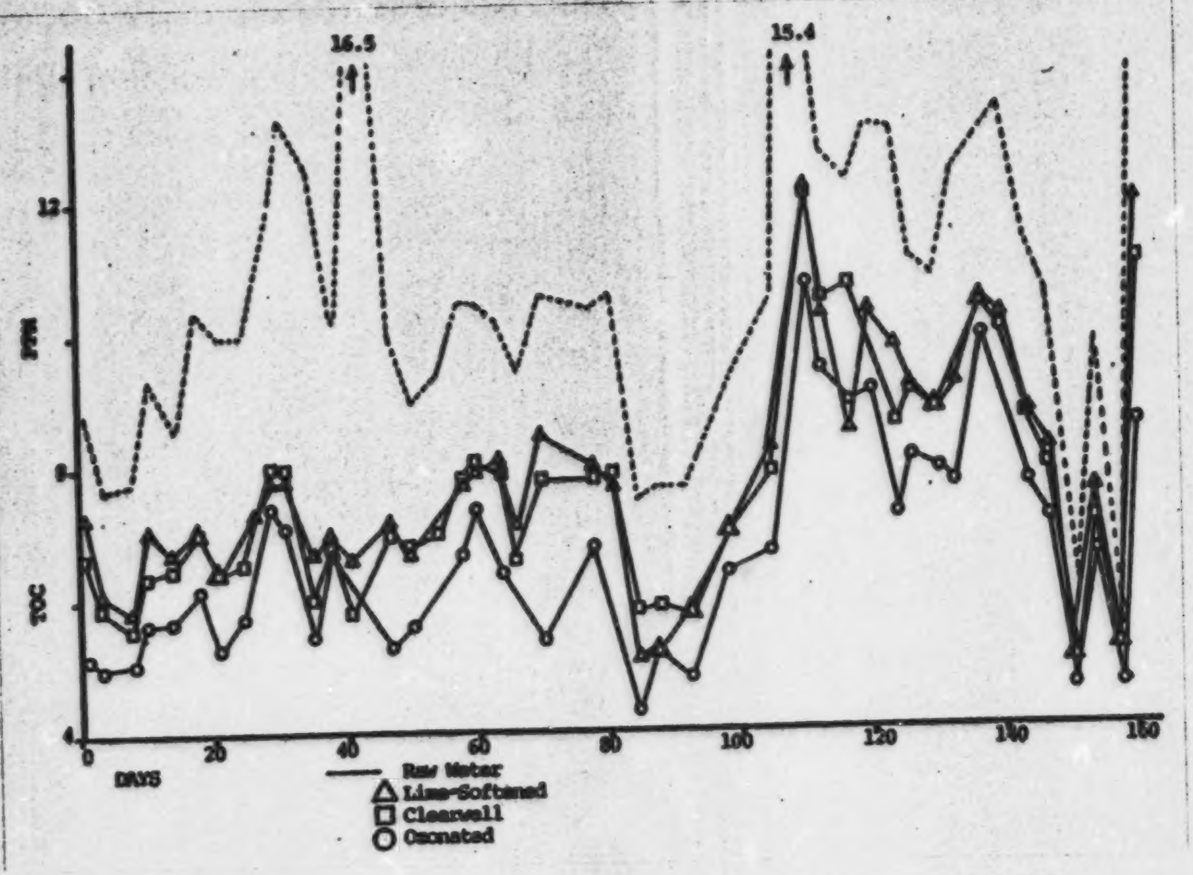


Figure 4. TOC profile of Sections I and II of the pilot plant.

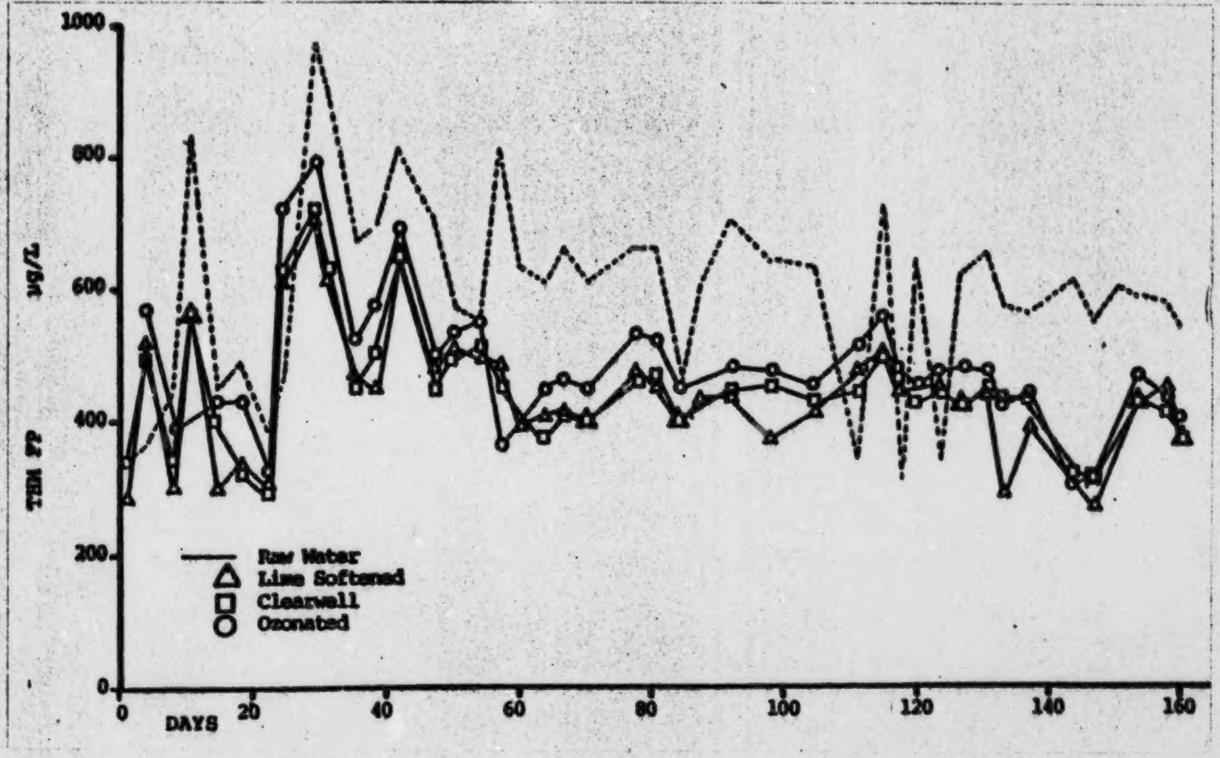


Figure 5. THMFP profile of Sections I and II of the pilot plant.

minutes, the free ozone level was always zero. The ozone demand for our water was so high that to achieve the absorbed ozone dose level desired, we had to improve the transfer efficiency to treat adequately 25 gal of water per minute. To accomplish this, the stainless steel tank following the MOC, which was originally designed as an additional contact time reservoir for the MOC, was converted to a BOC, as described earlier. Retention time in the BOC was approximately 11.3 minutes. The overall transfer efficiency of the MOC-BOC series was 74 percent. Effluent water from the BOC averaged 0.02 mg/L of free ozone. Over the test period, the absorbed ozone dose averaged 11.3 mg/L (43 mg/gal). Before this research phase on ozone-BAC, we studied the absorbed ozone dose required for Preston plant lime-softened water to produce a given free ozone level (mg/L) after 5 minutes of contact time. Results are shown in Figure 6. Absorbed doses of 30, 52, and 60 mg/gal were required to produce free ozone levels (5-minute contact time) of 0.1, 0.3, and 0.5 mg/L, respectively. However, at the time this work was performed, the average level of TOC in the raw water and lime-softened water were 8.3 and 5.8 mg/L, respectively. Thus the lime-softened water at that time contained approximately 26 percent less TOC than at present. In PS 1, the absorbed ozone dose in the MOC (54 percent transfer efficiency) was 32.8 mg/gal, and when the effluent (2.8-minute contact time and 0.88 mg/L free ozone) was held 2.2 minutes longer (5-minute contact time), the free ozone level was always zero. In the earlier work, with 26 percent lower TOC, an absorbed ozone dose of 32.8 mg/gal would have resulted in a free ozone level of approximately 0.12 mg/L after 5 minutes (see Figure 6).

### TOC—

The level of TOC entering the ozone contactors is plotted in Figure 4 (labeled clearwell). The level of TOC in the MOC-BOC effluent is also plotted in Figure 4 (labeled ozonated). Over the full test period, the average level of TOC in the ozone-contactor effluent was 6.7 mg/L, compared with the average entering value of 7.7 mg/L. Thus ozonation reduced the TOC level at the absorbed ozone dose applied (11.3 mg/L or 43 mg/gal) by 13 percent. The significance of these data must be interpreted in view of the actual pilot plant environment, where no single experimental factor remains constant. For example, the absorbed ozone dose data are plotted in Figure 7, with notation of average dose and average TOC level entering the contactors for test day 0 to 98 and 98 to 160. The overall average dose and TOC values for the full 160-day period are included. From day 0 to 98, the average TOC entering the contactors was 6.9 mg/L, and the average absorbed ozone dose was 10.9 mg/L. From day 98 to 160, the respective values were 8.9 and 12.3 mg/L. The overall 160-day average values were 7.7 and 11.3 mg/L. From day 0 to day 98, the percent reduction in TOC (caused by ozonation) was 13.3; from day 98 to 160, the percent reduction was 11.4; and the 160-day average was 12.5 percent reduction. The pH of the water entering the contactor did not change significantly. It would be difficult to conclude fine points from these data. For example, we cannot conclude whether or not the absorbed ozone dose increased because of an increase in TOC level, or because of addition of oxygen in the same period, or for some other reason. But we believe that the absorbed dose will increase under the same conditions as the TOC level increases.

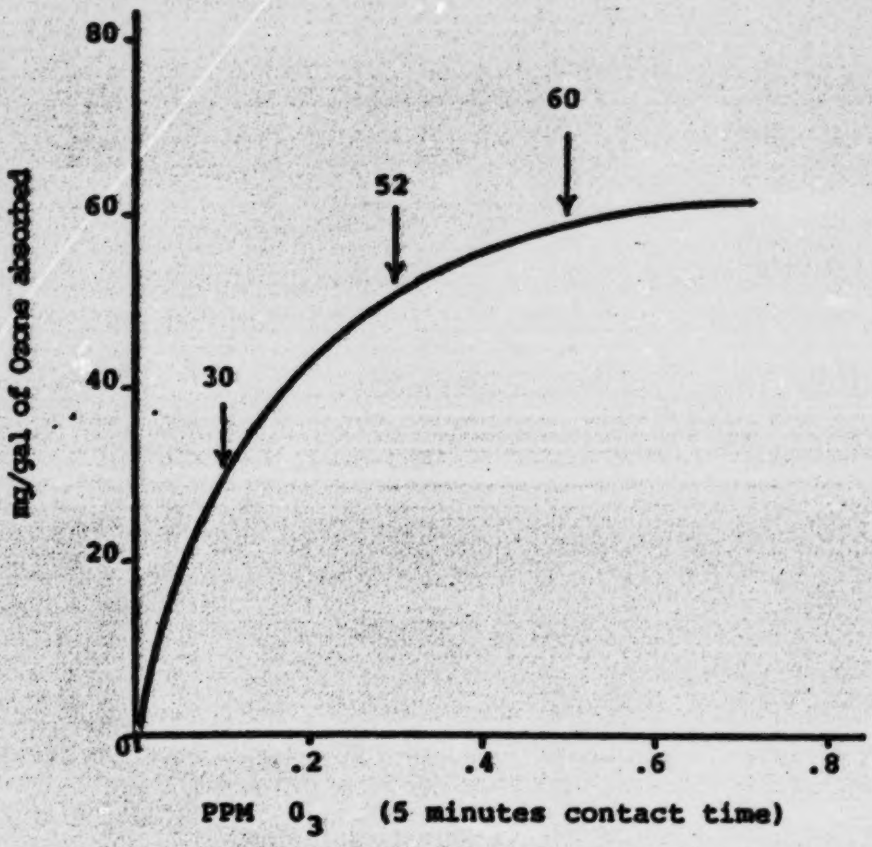


Figure 6. Absorbed ozone dose required by Preston plant lime-softened water (when TOC level averaged 5.8 mg/L) to produce a given free ozone concentration after 5 minutes of contact time.

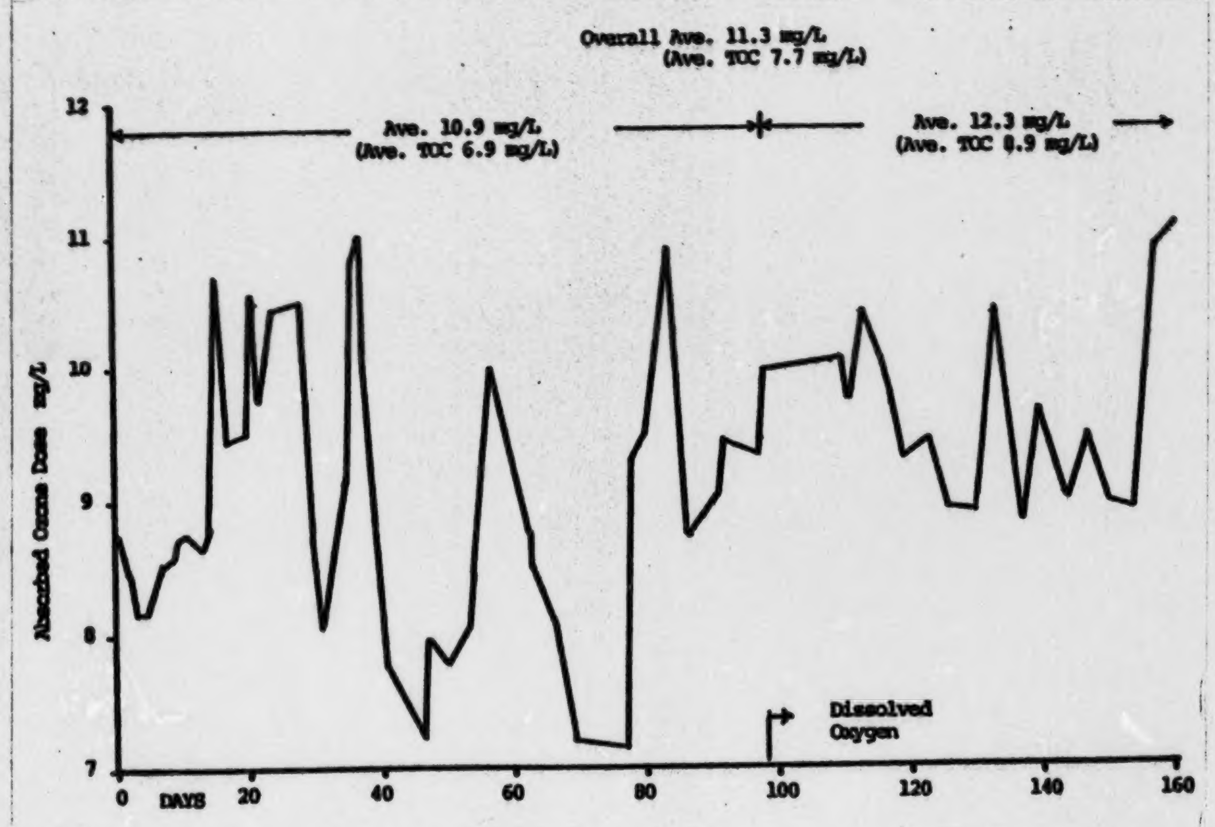


Figure 7. Absorbed ozone dose (mg/L) over test period.

### THMFP—

The THMFP levels entering and leaving the ozone contactors are plotted in Figure 5. Average values were 438 and 467 µg/L, respectively. If this difference is considered significant, ozonation increases the THMFP by approximately 7 percent (it is possible that the difference is not significant).

### Halogenated Organics—

The average concentration (µg/L) of halogenated organics in and out of the ozone contactors is shown in Table 4.

TABLE 4

AVERAGE CONCENTRATION (µG/L.) OF HALOGENATED
ORGANICS IN AND OUT OF THE OZONE CONTACTORS

| Compound | Entering Ozone Contactors | Leaving Ozone Contactors | After Air Only | % Remaining After Air Only |
|---|---|---|---|---|
| Vinyl Chloride | 7.4 | 0.0 | 4.1 | 55 |
| Methylene Chloride | 0.34 | 0.25* | - | - |
| Trans 1,2-Dichloroethene | 0.73 | 0.0 | 0.64 | 87 |
| 1,1-Dichloroethane | 1.6 | 1.7 | 1.5 | 88 |
| Cis 1,2-Dichloroethene | 21.5 | 0.25 | 18.7 | 87 |
| Chloroform | 0.8 | 0.4** | - | - |
| Trichloroethylene | 0.33 | 0.04 | 0.3 | 90 |
| Bromodichloromethane | 0.0 | 0.0 | 0.0 | 00 |
| Tetrachloroethylene | 0.0 | 0.0 | 0.0 | 00 |
| Chlorodibromomethane | 0.0 | 0.0 | 0.0 | 00 |
| Chlorobenzene | 0.41 | 0.0 | 0.34 | 82 |
| Bromoform | 0.0 | 0.0 | 0.0 | 00 |
| p-Chlorotoluene | 0.0 | 0.0 | 0.0 | 00 |
| m-Dichlorobenzene | 0.0 | 0.0 | 0.0 | 00 |
| p-Dichlorobenzene | 0.3 | 0.0 | 0.24 | 80 |
| o-Dichlorobenzene | 0.3 | 0.0 | 0.23 | 77 |

* Average from first 21 days of this period.
** Present only during first 24.3 test run days.

Reduction in concentration of these compounds in the contactors can result from two modes: (1) aeration and (2) destruction of the parent compound by ozonation. Table 4 reflects the response by both modes. To obtain the latter, the voltage on the ozonation cell was reduced to zero, allowing the normal volume of air (without ozone) to pass through the contactors. Results for individual compounds are described as follows.

## Chloroethylenes

Aeration alone reduced vinyl chloride concentration from 7.4 to 4.1 μg/L, a reduction to 55 percent of its entering value. Aeration plus oxidation by ozone reduced the concentration to zero. Previous works on a small-scale unit before this research phase produced the same results, and these results are as expected, based on the work of Hoigne and Bader (Ref. 38). In their Figures IIA and III, they show the reaction time necessary to reduce a solute to 37 percent (1/3) of its initial concentration, both in chloroform and water as the solvents, by reaction with $O_3$ or the OH· radical. They include reaction rates for chloroethylenes, except vinyl chloride, and for chloroform, chlorinated benzenes, etc. The reaction rate for the chloroethylenes decreases rapidly as the number of chlorine atoms increases. The dichloroethylenes react in a few seconds, and ethylene itself reacts in less than a second. One therefore might expect that vinyl chloride may also react rapidly. This was confirmed by the data in Table 4. Rapid decomposition of trans and cis 1,2-dichloroethylene, and even trichloroethylene, was also confirmed.

## Haloalkanes

The only chloromethanes present were the low levels of methylene chloride and chloroform, measured during the first 3 to 3 1/2 weeks of operation.

The reduction in concentration of these compounds by aeration alone was not determined. However, after ozonation, 74 percent of the methylene chloride and 50 percent of the chloroform was still present. Hoigne and Bader (Ref. 38) indicated long reaction times for these compounds. Our findings seem to confirm their findings, although our data for these two compounds are limited. We suspect that most or all of the losses recorded on these two compounds in Table 4 was the result of aeration.

The level of 1,1-dichloroethane in water entering the ozone contactors was 1.6 μg/L (Table 4). After ozonation, the level was essentially the same. Aeration alone may have removed some. The lack of reduction by ozonation of this compound was as expected.

The likelihood of ozone reacting with halide ions to form free halogens will also be discussed here. Some researchers have expressed the possibility of some free bromine formation. Rice, R.G., et al. (Ref. 39) summarize many references stating that ozonation of sea water produces hypobromous acid and bromoform. A conclusion was given that if a non-marine water containing both bromide and organic matter was ozonized, bromine-containing organic compounds would be formed. Umphres, M.D., et al. (Ref. 40) concluded that ozone does not form THM's either directly or through the oxidation of bromide.

## TABLE 5

## POTENTIAL VOLTAGE FOR ELECTROCHEMICAL EQUATIONS

| | Equation | | Potential Volts | | |
|---|---|---|---|---|---|
| 1. | $O_3+H_2O+2e^-\rightarrow O_2+2OH^-$ | 1.24 | 1+2 | 1+3 | |
| 2. | $2Cl^- \rightarrow 2e^- + Cl\uparrow_2$ | -1.36 | -0.12 | - | - |
| 3. | $2Br^- \rightarrow 2e^- + Br_2$ | -1.09 | - | 0.15 | - |
| 4. | $2I^- \rightarrow 2e^- + I_2$ | -0.54 | - | - | 0.7 |

OVERVOLTAGE = 0.2

From Table 5, with a negative potential of -0.12, ozone would not form free chlorine from $Cl^-$. With a positive potential of 0.15 volts, ozone would probably not form free bromine from $Br^-$. One reason might be that though the potential is a positive 0.15 volts, each reaction must overcome an overvoltage effect. This voltage, in excess of theoretical, is variable for each reaction, but a value of 0.2 volts is common. This would put the $Br^-$ potential voltage in the slightly negative region. At the pilot plant, it was demonstrated every day that free bromine was not formed. If any bromine was formed, it would react rapidly with precursors to form bromomethanes, and these compounds were never detected in the contactor effluent. Thus it appears that ozone under conditions existing in the pilot plant did not form free bromine in practice. It is even more unlikely that this reaction would occur as long as there are high concentrations of organic molecules present (TOC) with favorably high positive potentials, which was the case. On the other hand, in Table 5, the potential for ozone to change $I^-$ to free iodine is a positive 0.7 volts. This reaction takes place readily, even with organic molecules present, and is the KI-starch assay method for determining ozone.

### Chlorinated Benzenes

In Table 4, data show that low levels of chlorobenzenes, both mono and di, were readily eliminated by ozonation and not by aeration. This was expected based on the Hoigne and Bader work.

### Color—Units of Apparent Color

The average color of the water entering and leaving the contactors was 11 and 2, respectively (Table 1). Thus the ozone was as effective as (or slightly more so than) chlorine in removing color (breakpoint chlorination reduced the color to 3). Finished water leaving the Preston plant averages 4 color units.

pH

The average pH of the water entering and leaving the contactors was 8.5 and 8.0, respectively. Thus ozonation appeared to lower the average pH by 0.5.

Turbidity-NTU

The average turbidity of the water entering and leaving the contactors was 0.4 and 0.22, respectively.

Effect of pH on Ozonation of TOC and THMFP

A study was designed to determine what effect pH might have on ozonation of TOC and THM precursors. This work was done with the pilot plant equipment, varying the pH of the influent water to the ozone contactors, and measuring the effect on ozone concentration, transfer efficiency, TOC, and THMFP. The results are shown in Table 6.

TABLE 6

EFFECT OF pH ON OZONATION OF TOC AND THMFP

| pH | Free Ozone MOC Effluent | Free Ozone BOC Effluent | Absorbed Ozone Effluent | % Transfer Efficiency | % Change In THMFP | % Change In TOC |
|---|---|---|---|---|---|---|
| 7.0 | 1.27 | 0 | 13.02 | 69 | +6 | -6 |
| 8.5 | 0.67 | 0 | 14.63 | 77 | +0.5 | 0 |
| 10.0 | 0.0 | 0 | 15.89 | 84 | -14.0 | -14 |

Notice that with increasing pH, the level of free ozone in the MOC effluent decreased, and the transfer efficiency and absorbed ozone dose increased. Also, the level of THMFP showed an increase at pH 7, but a decrease of 14 percent at pH 10. The TOC data could be erratic but may indicate increased reduction of TOC with increasing pH. This was only one experiment with imperfect controls. We do not know whether these results are due to different chemical reactions at various pH ranges ($O_3$ versus -OH· free radical, for example), or the result of greater absorbed ozone dosage, or both. Two additional experiments were run in the laboratory under more controlled conditions. In a closed-loop purging system, equal levels of ozone were purged through water at pH levels of 7, 8.5, and 10. The closed-looped purging time necessary to obtain 100 percent transfer efficiency varied and increased with decreasing pH (the purging time was continued until no oxidant, $O_3$ or OH· radical remained in the water). In both experiments, with absorbed ozone dosage in the pilot plant usage range, no change was found in levels of either TOC or THMFP. This may suggest that the results in Table 6 are caused by the increased absorbed ozone dose. More study was needed on the effect on pH and the effect of absorbed ozone dose on TOC and THMFP. This work was done in the second pilot plant study (see Section 6).

Miller, G. W., et al. (Ref. 41) discusses the effectiveness of ozone treatment in Europe for organic removal where the applied ozone dose averages less than 3 mg/L, with correspondingly low TOC levels. Our applied dose of 12 mg/L may appear high, but in reality may be far too low for our water. We may find that for significant TOC or THMFP reduction or modification, we need levels equal to or greater than our present chlorine demand for breakpoint chlorination (18 mg/L and rising as we extend the well fields further west into the Everglades).

## Pilot Plant Section III Chemical Data

### Halogenated Organics—

#### Vinyl Chloride

The average level of vinyl chloride in water from the clearwell was 7.4 µg/L. This level was reduced to zero in the ozone contactors, therefore no vinyl chloride reached the ozone-BAC tower. The vinyl chloride entering the sand control tower passed through with no reduction. In the nonozone-BAC tower, at the 2.5, 5 and 10 ft. levels, vinyl chloride breakthrough and saturation occurred at run days 3.5, 24.3 and 29, 21, 54 and 54, respectively.

#### Cis 1,2-dichloroethene

Clearwell water averaged 22 µg/L cis 1,2-dichloroethene. The ozone contactors reduced this level to 0.25 µg/L. In the ozone-BAC tower, 2.5 ft. removed this low level to test run day 13.7. On test day 140, 14.8 µg/L was detected, suggesting roll-over. To the end of the test, 160 days, at the 2.5-ft. sample port, decreasing levels were detected. On test day 140, the high-level discharge observed at 2.5 ft. was also seen at 5 and 10 ft., but at lower concentrations.

The sand tower did not inhibit the passage of the compound. In the nonozone-BAC tower at 2.5, 5 and 10 ft., breakthrough occurred at 24, 24 and 57 days, respectively. At 2.5 ft., one-half saturation was reached at day 137 and discharge continued at this rate to test day 151, after which low-level passage occurred. At 5 ft., saturation occurred at day 158, and at 10 ft., saturation occurred at day 158.

#### Trans 1,2-dichloroethene

Clearwell water averaged 0.7 µg/L trans 1,2-dichloroethene, and this level passed through the sand tower. This concentration was reduced to zero by the ozone contactors. In the nonozone-BAC tower at 2.5, 5 and 10 ft., breakthrough occurred at 133, 151 and 151 days, respectively. At 2.5 ft., saturation occurred at 154 days.

1,1-Dichloroethane

Clearwell water averaged 1.6 µg/L 1,1-dichloroethene. The highest concentration observed during the test was 34 µg/L. In the previous 5 years of research testing at the Preston plant, the average and highest recorded values were 0.6 and 1.1 µg/L, respectively.

Again, the sand tower passed the compound. The clearwell concentration was essentially unchanged by the ozone contactors. In the ozone-BAC tower at 2.5, 5 and 10 ft., breakthrough and saturation ocurred at 35, 64 and 98 days, and 113, 123 and 158 days, respectively. In the nonozone-BAC tower, the respective values were, 41, 91 and 98 days, and 105, 117 and 137 days.

Trichloroethylene

Clearwell water averaged 0.33 µg/L trichloroethylene. The ozone contactors reduced the average to 0.04. Both BAC towers allowed early breakthrough at a bed depth of 2.5 ft. Breakthrough at 10 ft. in the ozone- and nonozone-BAC towers was 70 and 117 days, respectively, with saturation at 70 and 151 days.

Dissolved Oxygen Profile of Pilot Plant—

As discussed earlier, for the first 98 days of the 160-day test period, no attempt was made to increase the DO at any bed-depth level to determine baseline results under anaerobic conditions. The DO profile of the pilot plant is shown in Table 7.

DO levels for raw water, lime-softened and clearwell effluent were 0.16, 0.47 and 0.5 mg/L, respectively. Clearwell water entered the sand tower and nonozone-BAC tower. Both of these towers at the 2.5, 5 and 10 ft. levels reduced DO to 0.14, 0.12 and <0.1, and <0.1, <0.1 and <0.1, respectively. The ozone contactors raised the DO level to 7.4 mg/L, the maximum level for our water at these conditions. At 2.5, 5, 7.5 and 10 ft., the ozone-BAC tower decreased the DO level to 0.94, 0.13, <0.1 and <0.1, respectively. Thus all towers were essentially anaerobic for the first 98 days. On test day 98, oxygen was added to all three towers, and for the remainder of the test all tower effluents averaged approximately 7 mg/L.

TOC—

Data plots of TOC levels in the clearwell and ozone contactor effluents are reported in Figure 8, which also shows the TOC level in the ozone-BAC tower at 2.5, 5 and 10 ft. Since the influent level of TOC varied quite widely, the data are presented as percent TOC breakthrough in Figure 9. Note that saturation was almost reached at the 2.5-ft. zone. Adding oxygen after test day 98 did not seem to influence the general shape of the curves. From test day 0 to approximately day 50, differences between the 2.5, 5 and 10 ft. zones are most pronounced. From test day 90 on, the differences between breakthrough curves narrows. Later, a numerical comparison of TOC and THMFP data for the two carbon towers will be made.

## TABLE 7

## PILOT PLANT DISSOLVED OXYGEN (mg/L) PROFILE

| Location | | DO, mg/L |
|---|---|---|
| Raw Water | | 0.16 |
| Lime-Softened Effluent | | 0.47 |
| Clearwell | | 0.5 |
| MOC-BOC Effluent | | 7.4 |
| Ozone-BAC Tower | 2.5 ft. | 0.94 |
| Ozone-BAC Tower | 5.0 ft. | 0.13 |
| Ozone-BAC Tower | 7.5 ft. | <0.1 |
| Ozone-BAC Tower | 10.0 ft. | <0.1 |
| Sand Tower | 2.5 ft. | <0.1 |
| Sand Tower | 5.0 ft. | <0.1 |
| Sand Tower | 10.0 ft. | <0.1 |
| Nonozone-BAC Tower | 2.5 ft. | <0.1 |
| Nonozone-BAC Tower | 5.0 ft. | <0.1 |
| Nonozone-BAC Tower | 10.0 ft. | <0.1 |

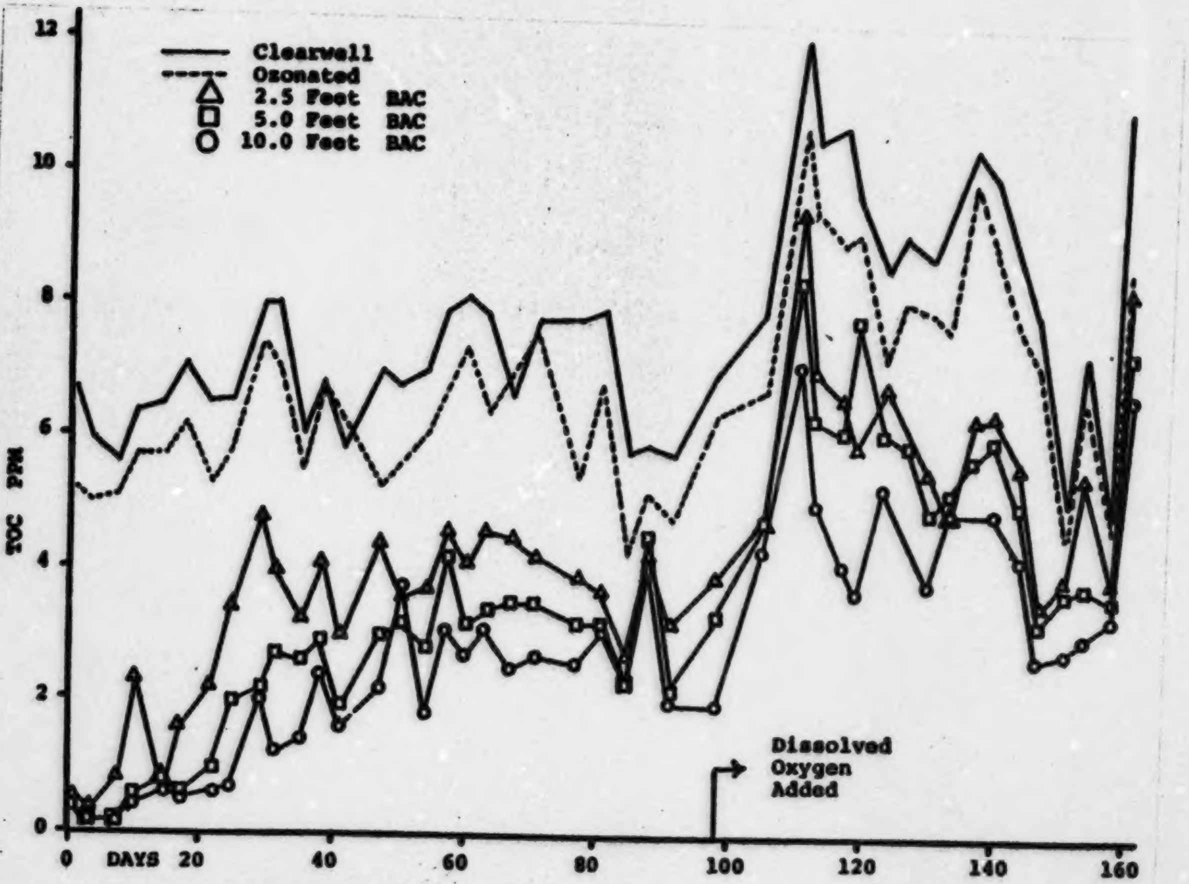


Figure 8. TOC profile in the ozone-BAC tower.

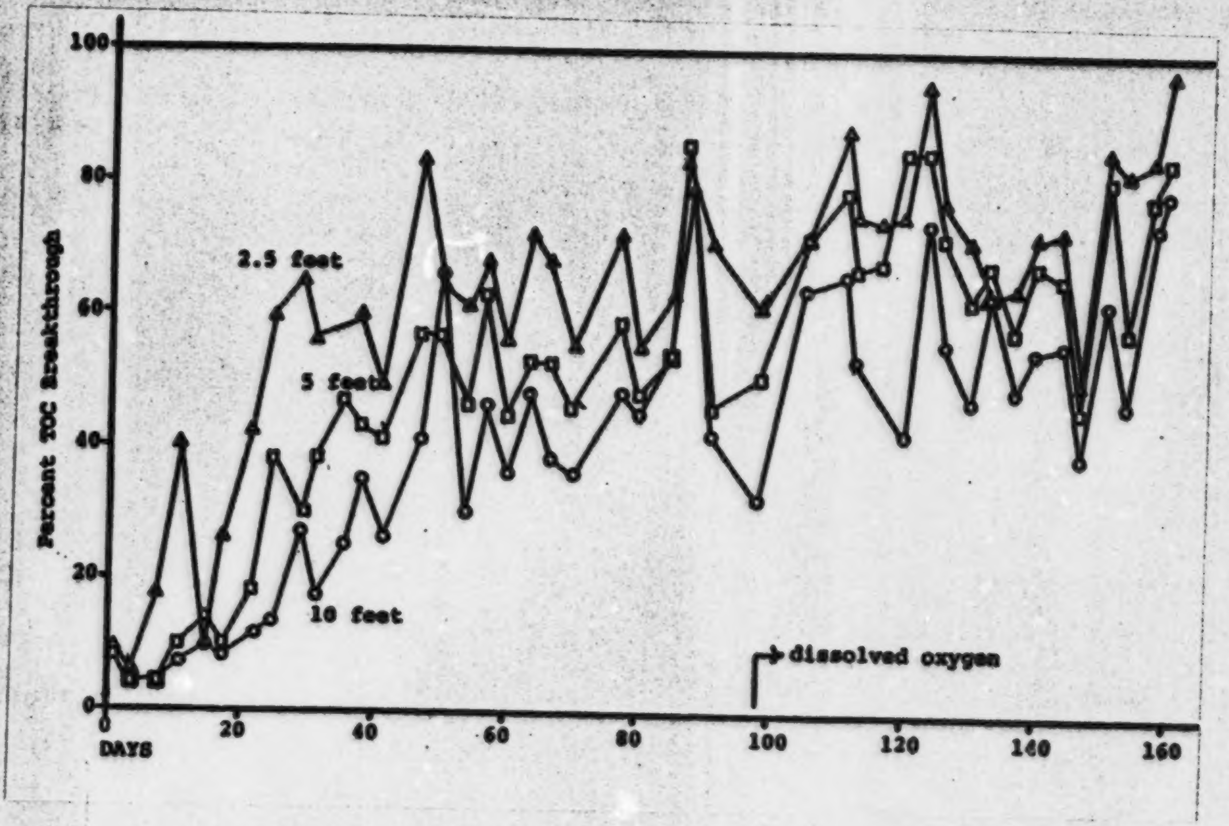


Figure 9. Percent TOC breakthrough in the ozone-BAC tower.

The TOC profiles for the nonozone-BAC tower are shown in Figures 10 and 11. Again, the plots in Figure 11 make the profiles easier to follow. In this tower, saturation occurred for all three bed depths. This tower received 13 percent more TOC than the ozone-BAC tower (which was reduced 13 percent by ozonation). In Figure 11 at test day 151, TOC roll-over may have occurred. The test was not carried far enough to confirm this point. Making the tower aerobic after test day 98 did not seem to alter the breakthrough curves. The TOC data can also be considered when plotted as accumulated TOC results (Figures 12,13 and 14). Figure 12 shows the accumulated TOC in the influent to the control sand tower and the nonozone-BAC tower. The accumulated amount of TOC removed by 2.5, 5 and 10 ft. of the nonozone-BAC tower is also shown. The curve for the accumulated TOC removed by 2.5 ft. of BAC clearly levels off faster than the curve for 10 ft. of BAC. In Figure 12, the accumulated amount of TOC removed by 10 ft. of sand in the control sand tower is also shown. Up to test day 77, the sand tower passed slightly more TOC than entered (up to 1 or 2 percent). After test day 77, the sand tower began to show TOC removal. This condition was observed for all three bed depths. At 2.5 ft., the sand tower began to show TOC removal after test day 31. At 5 ft., removal began on test day 70. The bacteria associated with the sand tower may be responsible for the accumulated TOC removal shown in Figure 12. The surface of the sand may not be ideal for bacteria to fasten itself to, and one wonders how much TOC would be removed by a nonadsorbent solid tower packing whose surface favored bacterial attachment. Data on TOC removal by the sand tower will be discussed further when the data in Figure 14 are discussed. The accumulated TOC influent to the ozone-BAC tower is shown in Figure 13. Amounts of accumulated TOC removed by 2.5, 5 and 10 ft. of BAC are also shown. For comparison, the curves from Figure 12 (accumulated TOC removal by the nonozone-BAC and sand towers and their accumulated influent) are shown as dashed curves. The ozone-BAC tower received less TOC, but each bed depth removed more TOC than the nonozone-BAC tower. The adsorptive capacity of GAC has been shown to increase (Ref. 1) as the concentration of a substance increases. The ozone-BAC tower, receiving less TOC than the nonozone-BAC tower, removed more TOC. This result seems to contradict the above statement. However, it could be evidence that ozonation of the water does alter the TOC substances, making them more readily removed by the BAC tower.

In Figure 14, accumulated TOC removal (on the X-axis) is plotted versus accumulated TOC influent to each bed depth of tower. For each bed depth, the ozone-BAC tower removed more TOC than the nonozone-BAC tower. Data for the sand tower shows slightly more removal at the 2.5-ft. bed depth. The 10-ft. depth removed slightly more than the 5-ft. depth.

The daily level of TOC entering the sand tower is shown in Figure 15. The effluent TOC for each bed depth is also shown. The influent curve is shown by the heavy line. It is apparent that for an initial period of time, slightly more TOC was in the effluent compared with the influent. In general, from test day 31 to 77, the level of TOC was below the influent for all bed depths.

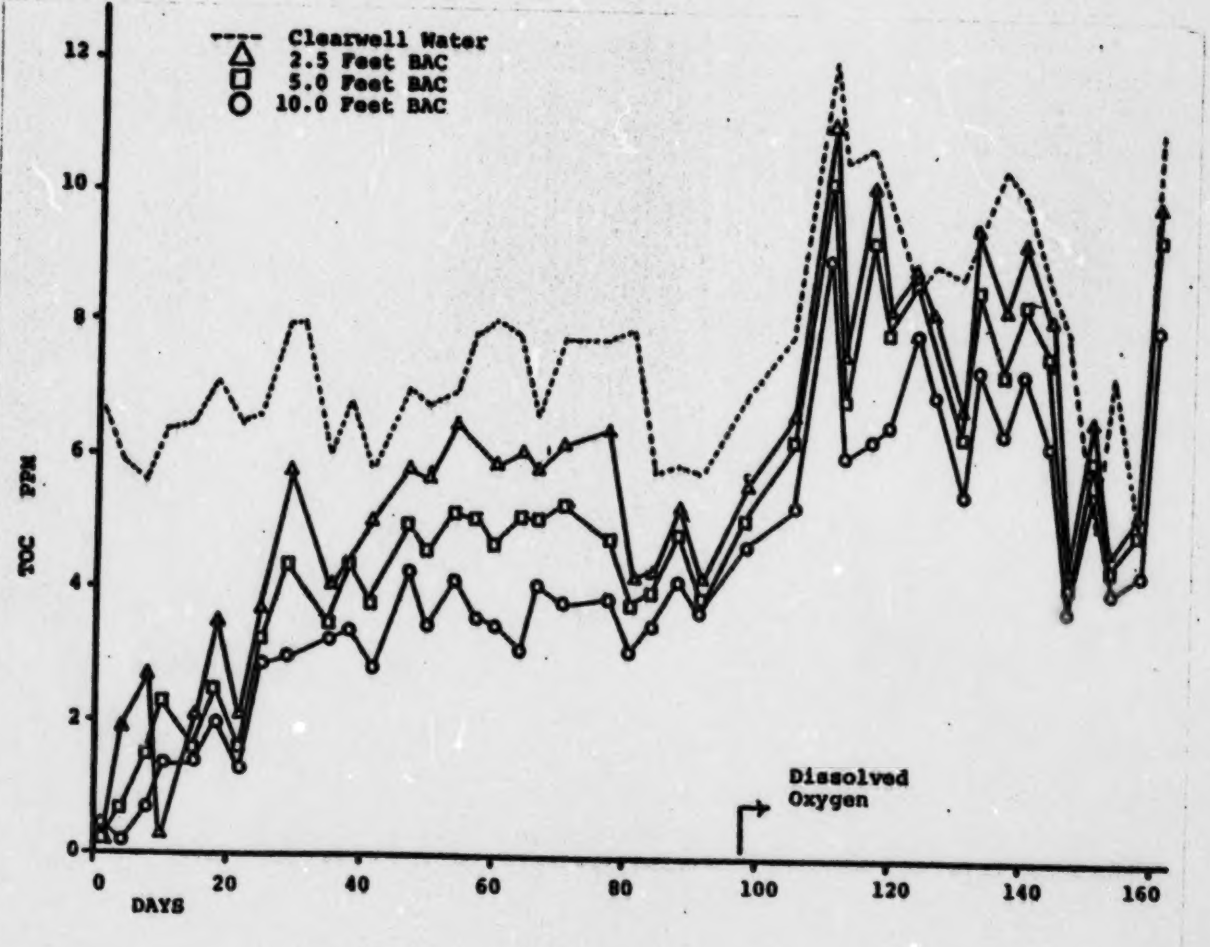


Figure 10. TOC profile in the nonozone-BAC tower.

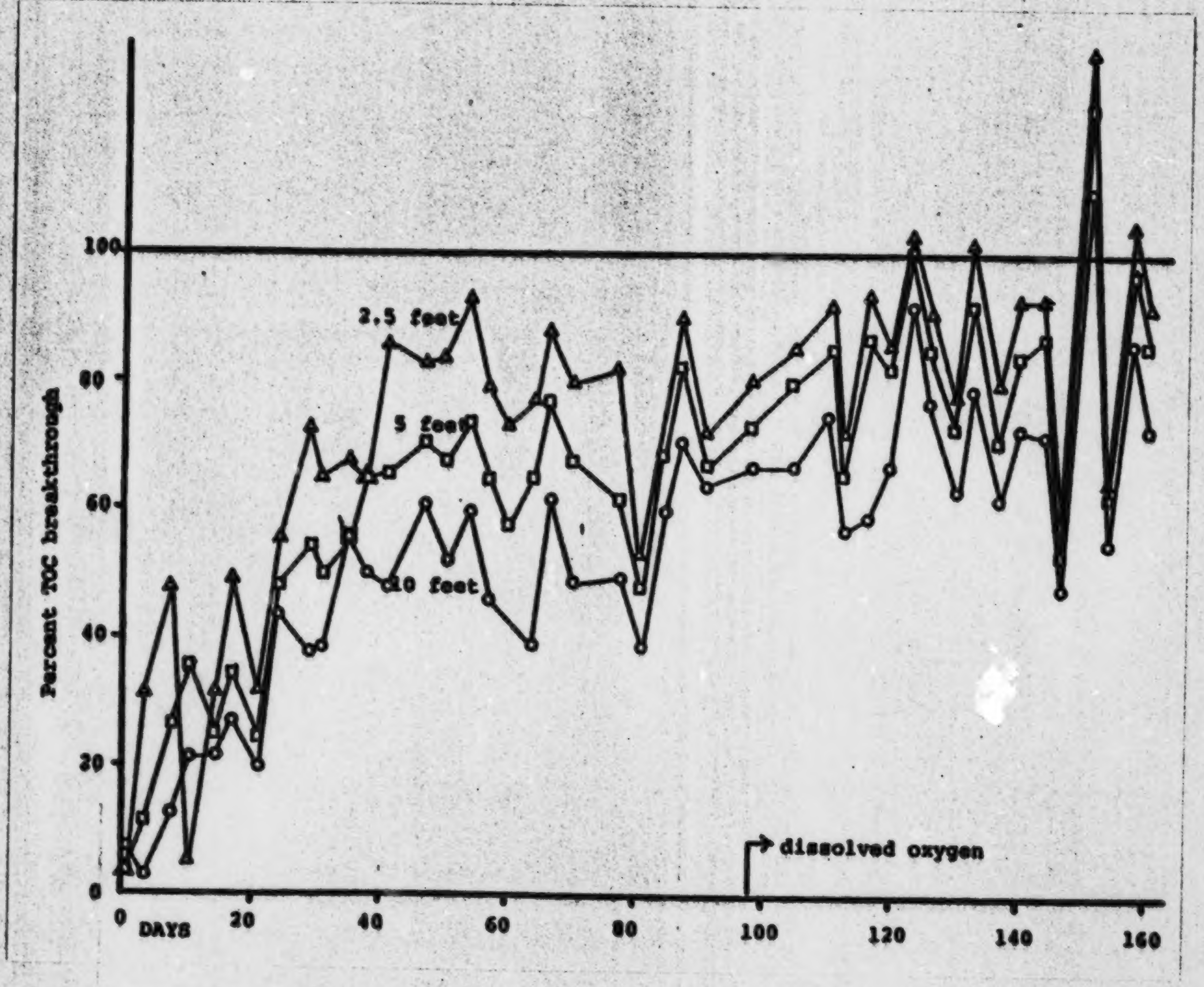


Figure 11. Percent TOC breakthrough in the nonozone-BAC tower.

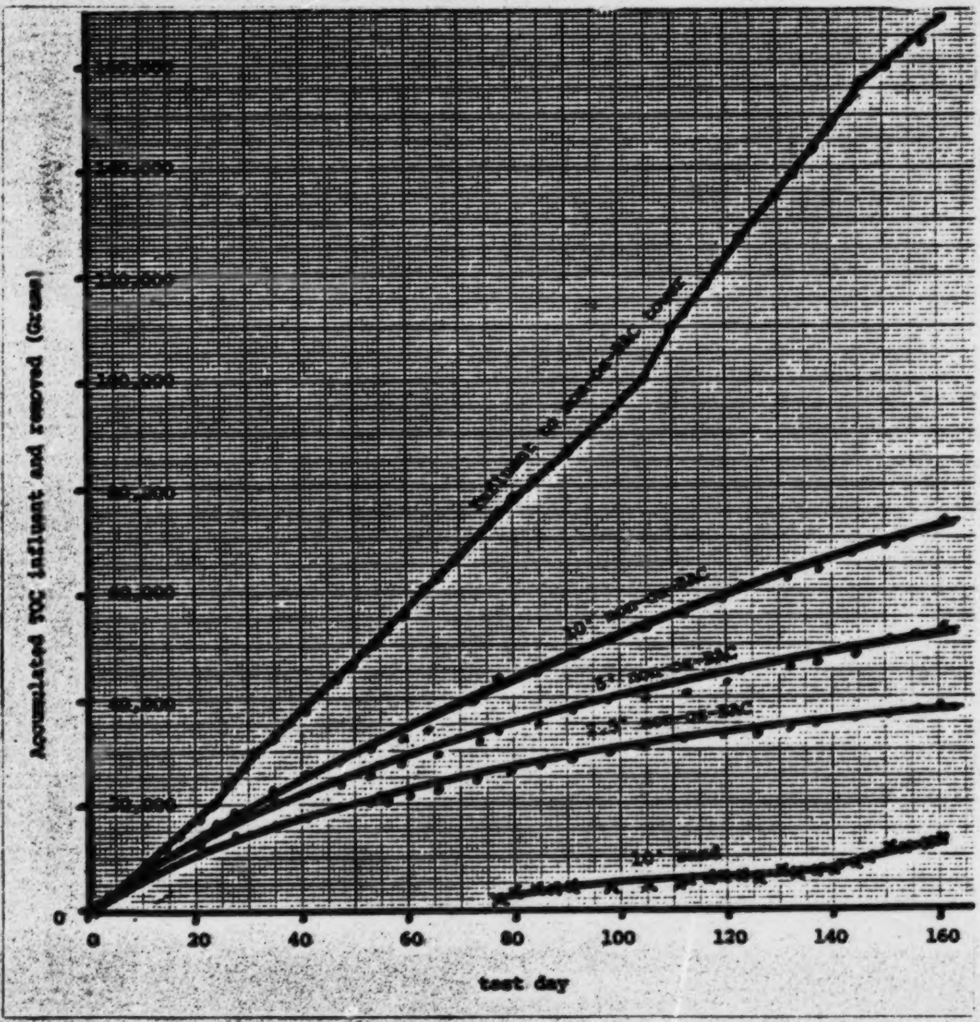


Figure 12. Accumulated TOC influent and removal by nonozone-BAC tower (PS 1).

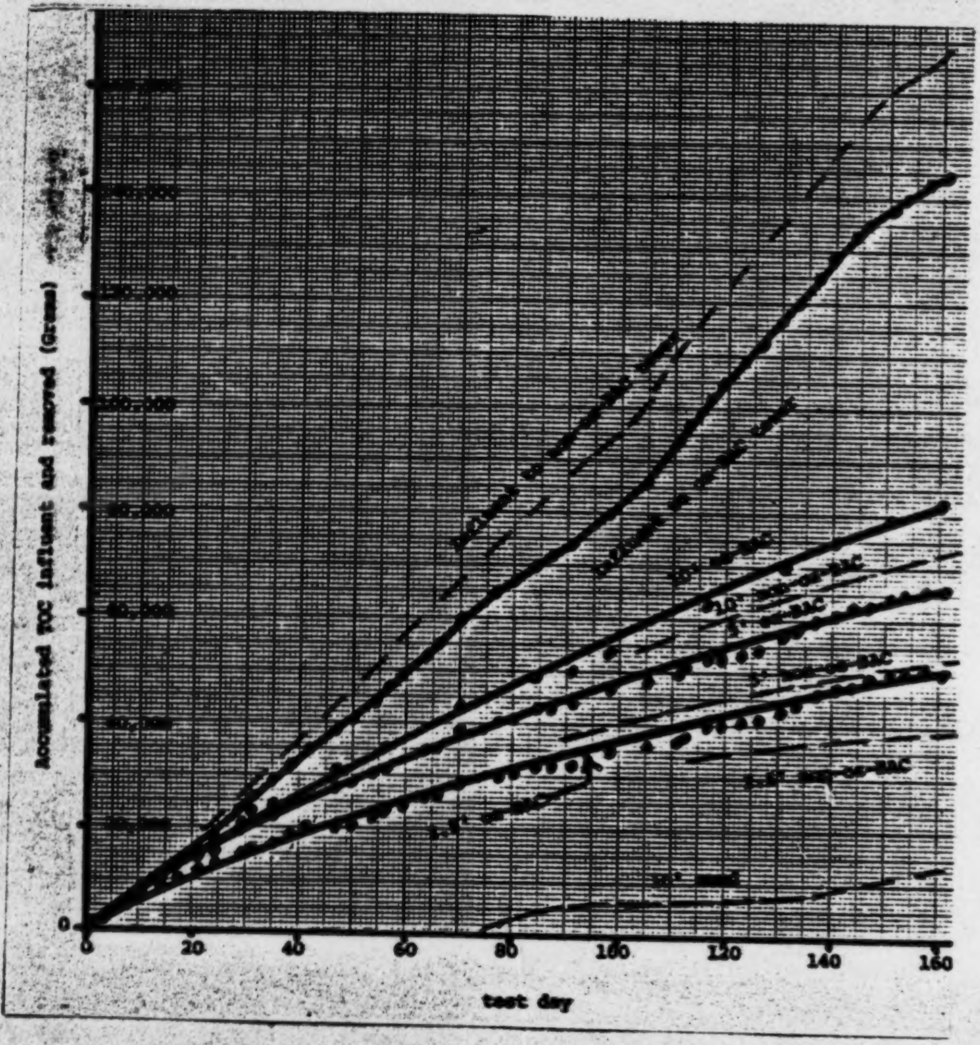


Figure 13. Accumulated TOC influent and removal by ozone-BAC tower (PS 1).

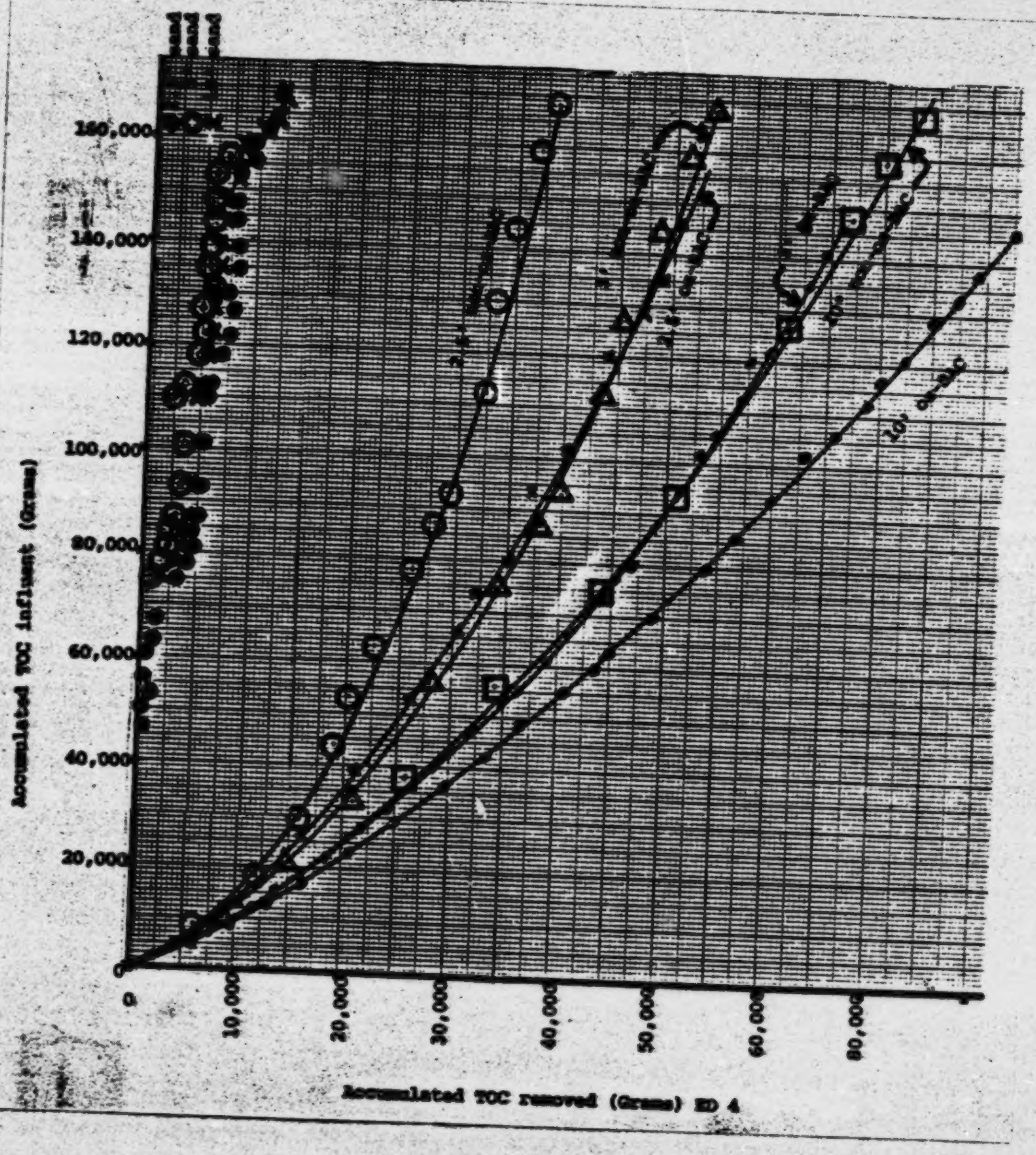


Figure 14. Plot of accumulated TOC influent corresponding with accumulated TOC removed by BAC tower (PS 1).

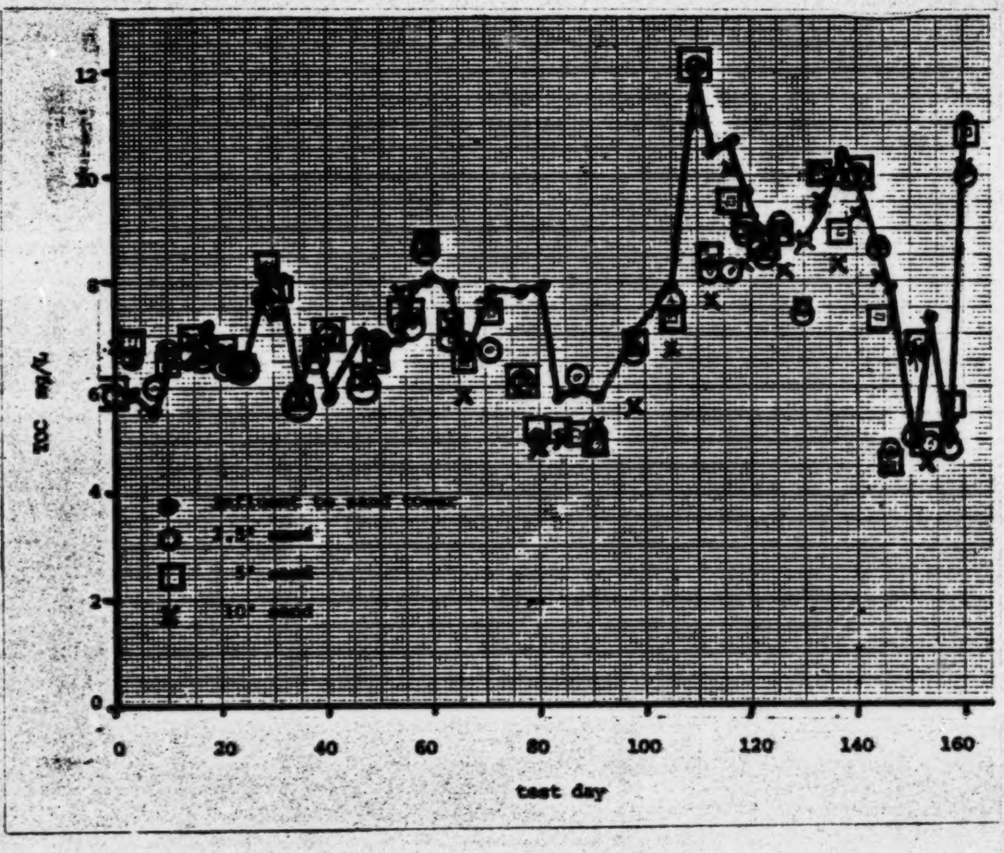


Figure 15. TOC influent and effluent (sand tower, PS 1).

### THMFP—

THMFP breakthrough curves and percent breakthrough curves for the ozone-BAC tower are presented in Figures 16 and 17. In this case, this tower received 7 percent more THMFP than the nonozonated-BAC tower (but still also received 13 percent less TOC). In Figure 17, saturation was reached at all three bed depths, and again, some roll-over may have occurred. Similar curves for the THMFP profile in the nonozone-BAC tower are shown in Figures 18 and 19. In Figure 19, THMFP saturation for all three bed depths occurred earlier. Again, some roll-over may have occurred.

At all bed depths, the sand tower essentially passed all the THMFP received. Again, adding DO after test day 98 did not appear to alter the course of the breakthrough curves.

### Comparison of the Two BAC Tower Systems—

The TOC and THMFP breakthrough curves for the two BAC tower systems just presented can be interpreted and compared in many ways. Two of them considered first are (1) days to a specific level of TOC and THMFP breakthrough and (2) a comparison of days to saturation. Comparison (1) was based on bed-life criteria developed in our previous work (Ref. 6) and discussed in Appendix A in this report. Referred to as Criterion 1, bed-life exhaustion occurs when 3 mg/L of TOC or 200 µg/L of THMFP breakthrough occurs. On this basis, 10 ft. of ozone- and nonozone-BAC are compared in Table 8.

TABLE 8

10-ft. BAC LIFE (DAYS) FOR CRITERION 1

| Parameter | No Ozone | Ozone |
|---|---|---|
| THMFP | 20 | 45 |
| TOC | 23 | 50 |

In this baseline anaerobic study, the THMFP and TOC bed life for the nonozone- and ozone-BAC towers were 20 and 23 days and 45 and 50 days, respectively. Thus ozone treatment increased the bed life by a factor of approximately 2.2.

Based on Criterion 2, above, days to saturation are expressed in Table 9.

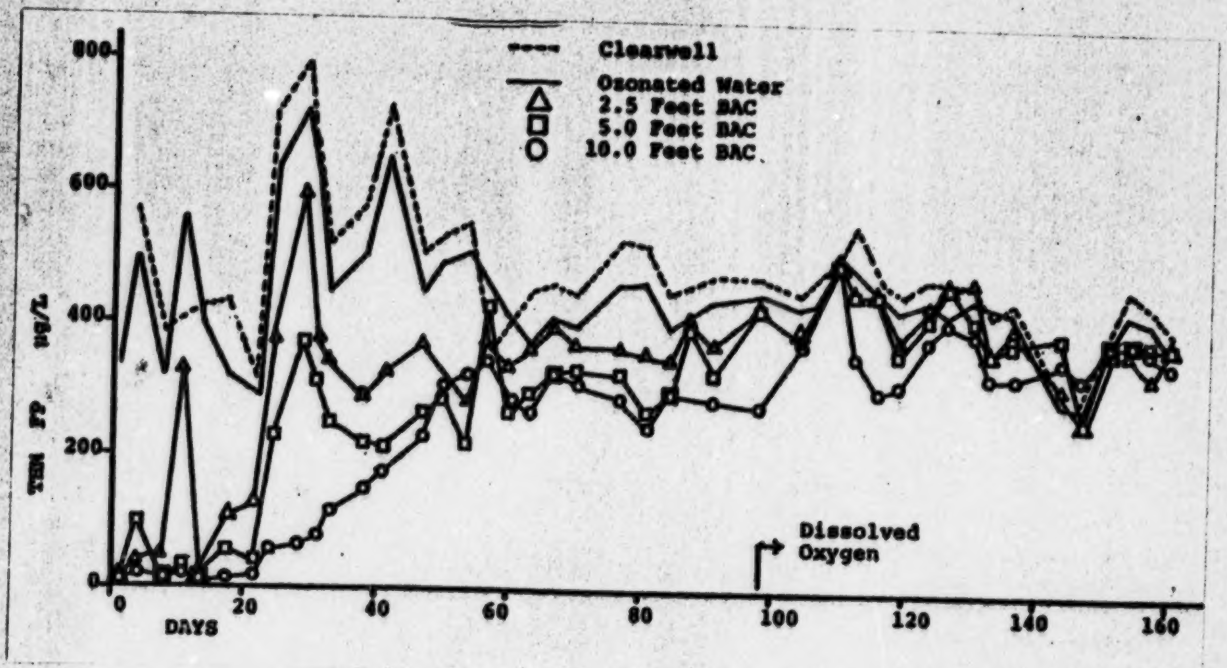


Figure 16. THMFP profile in the ozone-BAC tower.

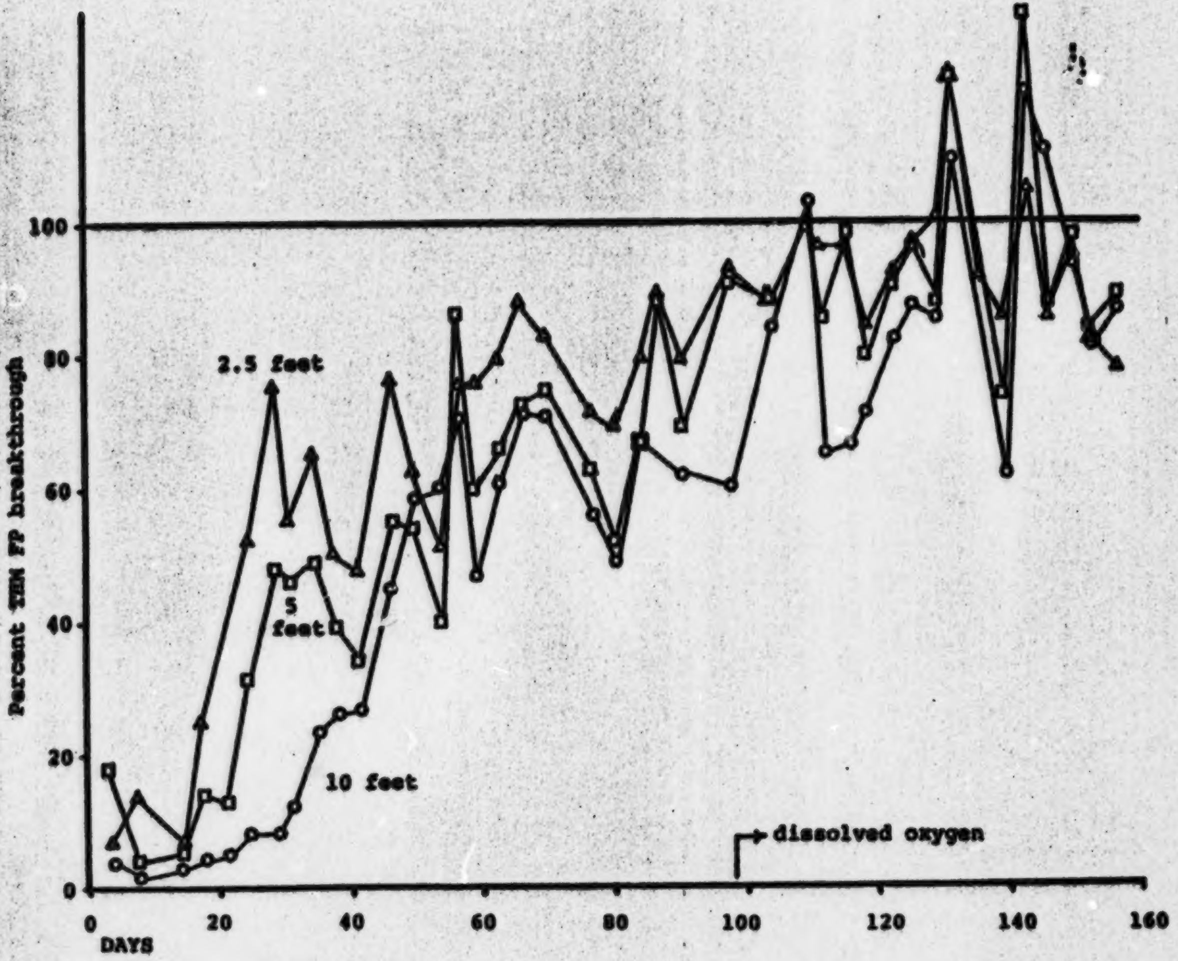


Figure 17. Percent THMFP breakthrough in the ozone-BAC tower.

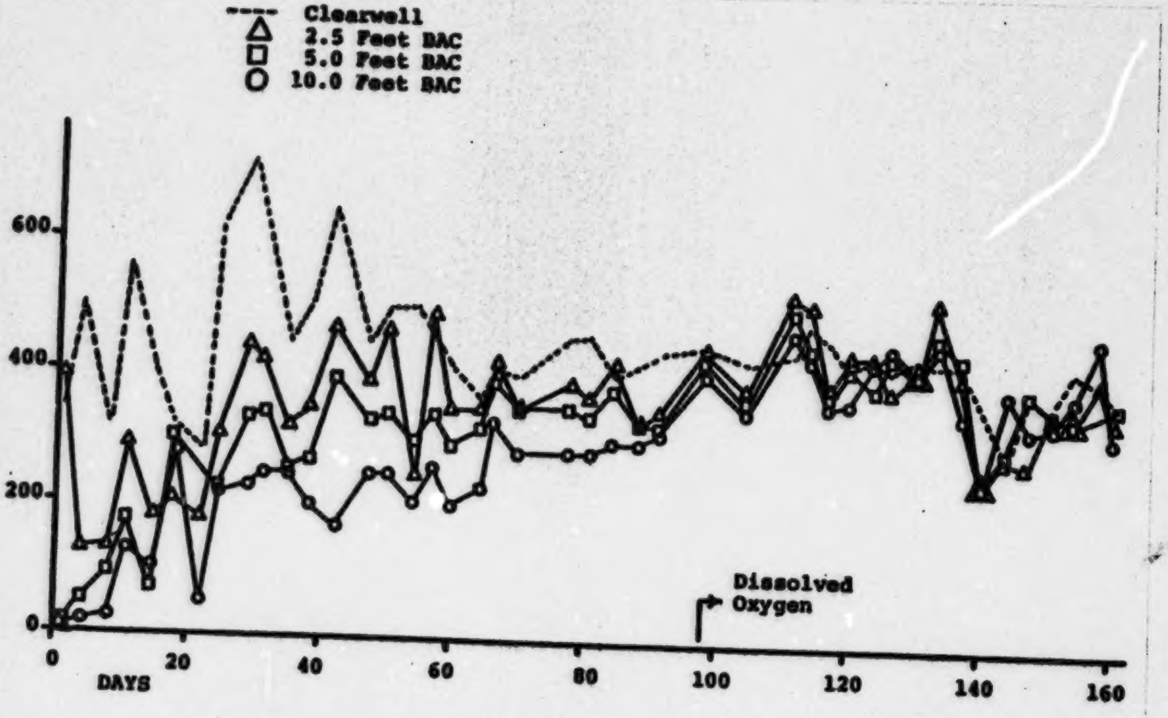


Figure 18. THMFP profile in the nonozone-BAC tower.

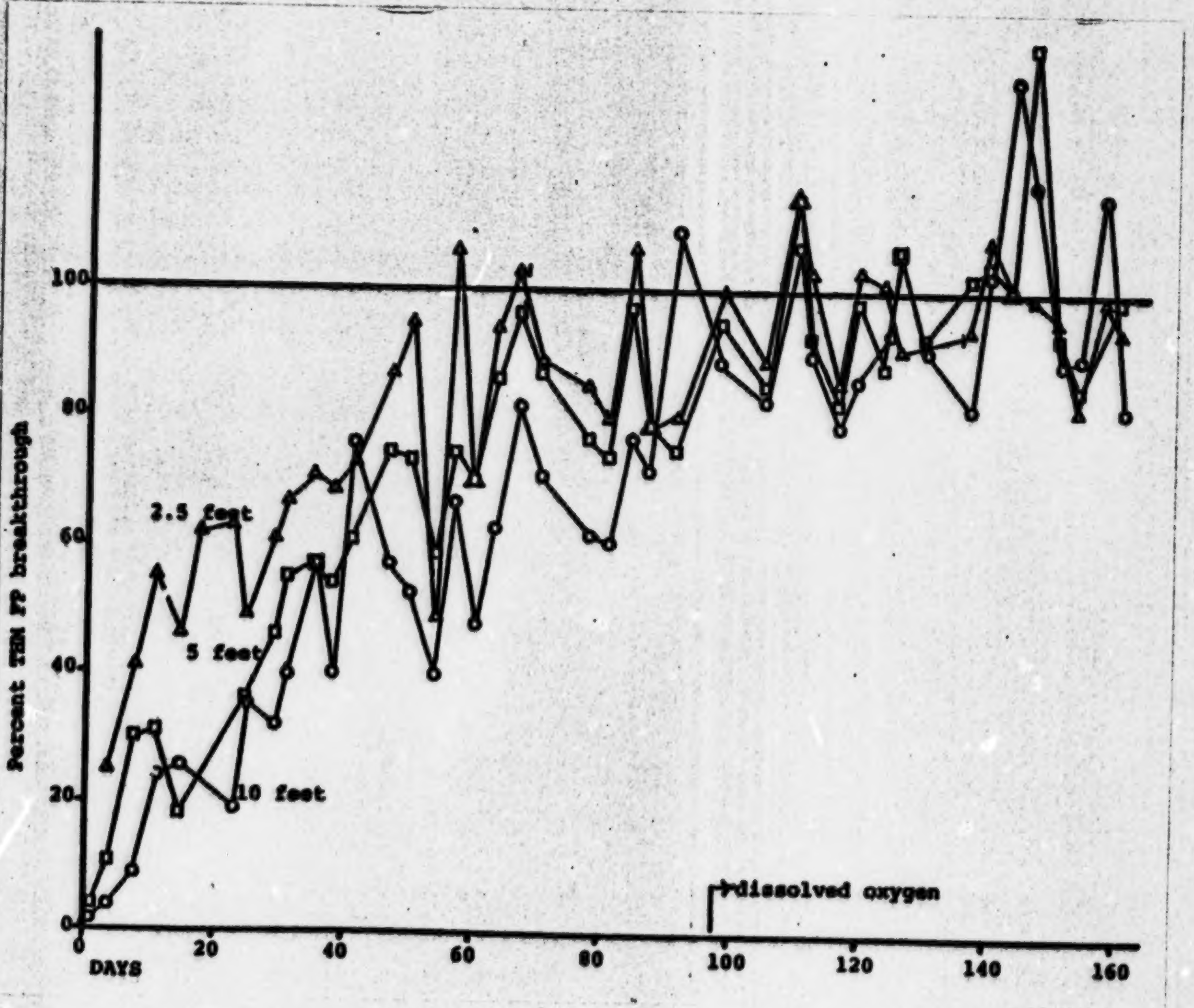


Figure 19. Percent THMFP breakthrough in nonozone-BAC tower.

## TABLE 9

## 10-FT. BAC SATURATION (DAYS) FOR CRITERION 2

| Parameter | No Ozone | Ozone |
|---|---|---|
| THMFP | 93 | 137 |
| TOC | 150 | estimated 221 |

In both cases (TOC and THMFP), ozonation extended saturation time by a factor of 1.5. In our opinion, Criterion 1 is more meaningful.

The two BAC tower systems can also be compared in another way. They should be compared as systems—that is, a comparison of the input and output of the control BAC tower versus the ozone-BAC tower, not the input and output of the BAC tower alone. A comparison of the two systems for each bed depth is shown in Figures 20, 21 and 22 for TOC, and in Figures 23, 24 and 25 for THMFP. The plotted points were obtained by dividing the effluent concentration from the ozone-BAC tower by the effluent from the nonozone-BAC tower for each bed depth and multiplying by 100 to give the percent difference.

Figure 20 shows that at the 2.5-ft. bed depth, the ozone-BAC tower system initially performed better than the nonozone-BAC tower system. On test day 3.5, the ozone-BAC tower passed only 16 percent of the TOC level passed by the nonozone-BAC tower. On test days 7.5, 10.5, 15 and 17, passage through the ozone-BAC tower increased, and on test day 21, the ozone-BAC tower passed 5 percent more TOC. For the remaining testing period, the ozone-BAC system averaged 75 percent TOC passage compared with the nonozone-BAC system. In Figures 20 through 25, the percent difference data points for TOC and THMFP for the first and second sampling days may show high percent differences. These first few sampling points are really insignificant and should be ignored when calculated in this way. For example, in Figure 20, the first sampling point on test day 0.5 shows that the ozone-BAC tower passed 250 percent as much TOC as the nonozone-BAC tower. The actual passage was 0.5 and 0.2 mg/L, respectively. Both values are very low compared with the approximately 8.5 mg/L influent.

In Figures 21 and 22, at 5 and 10 ft. of bed depth, the ozone-BAC tower performed better than the nonozone-BAC tower for increasingly long time periods before reaching a plateau region of better performance. At 5 ft., the plateau region was reached in approximately 31 days. For the remaining testing period, the ozone-BAC tower passed an average of 72 percent as much TOC as the nonozone-BAC tower. At 10 ft., the plateau region was reached in approximately 50 days. From test day 50 to 87, the plateau region may have been higher than for the remaining period. Average values were 80 and 68 percent, respectively.

$$\frac{\text{TOC effluent 2.5 ft. of ozonated BAC tower}}{\text{TOC effluent 2.5 ft. of nonozonated BAC tower}} \times 100 = \begin{array}{l}\text{Percent difference of} \\ \text{ozonated BAC Tower} \\ \text{compared to nonozonated} \\ \text{BAC Tower}\end{array}$$

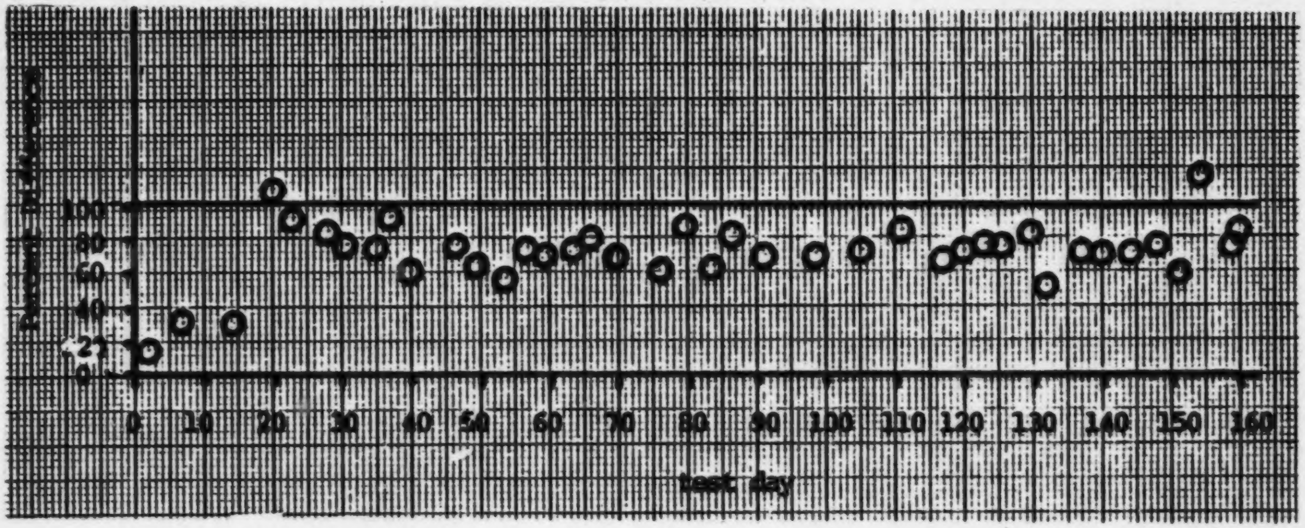


Figure 20. TOC effluent from 2.5 ft. of bed depth of ozone-BAC tower compared with TOC effluent from 2.5 ft. of bed depth of nonozone-BAC tower.

$$\frac{\text{TOC effluent 5 ft. depth ozonated BAC Tower}}{\text{TOC effluent 5 ft. depth nonozonated BAC Tower}} \quad X = \quad \begin{array}{l}\text{Percent Difference of}\\ \text{ozonated to nonozonated}\\ \text{effluent}\end{array}$$

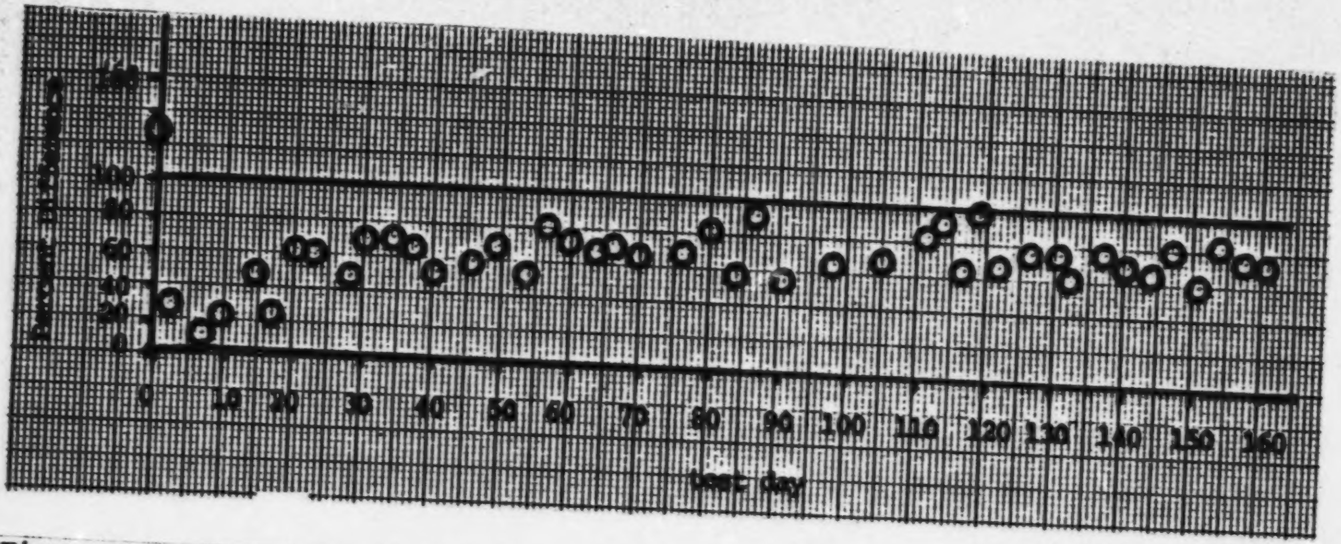


Figure 21. Percent difference of TOC levels of ozonated to nonozonated effluents from 5 ft. of BAC tower.

$$\frac{\text{TOC effluent 10 ft. depth ozonated BAC Tower}}{\text{TOC effluent 10 ft. depth nonozonated BAC Tower}} \times 100 = \text{Percent difference of ozonated to nonozonated effluent}$$

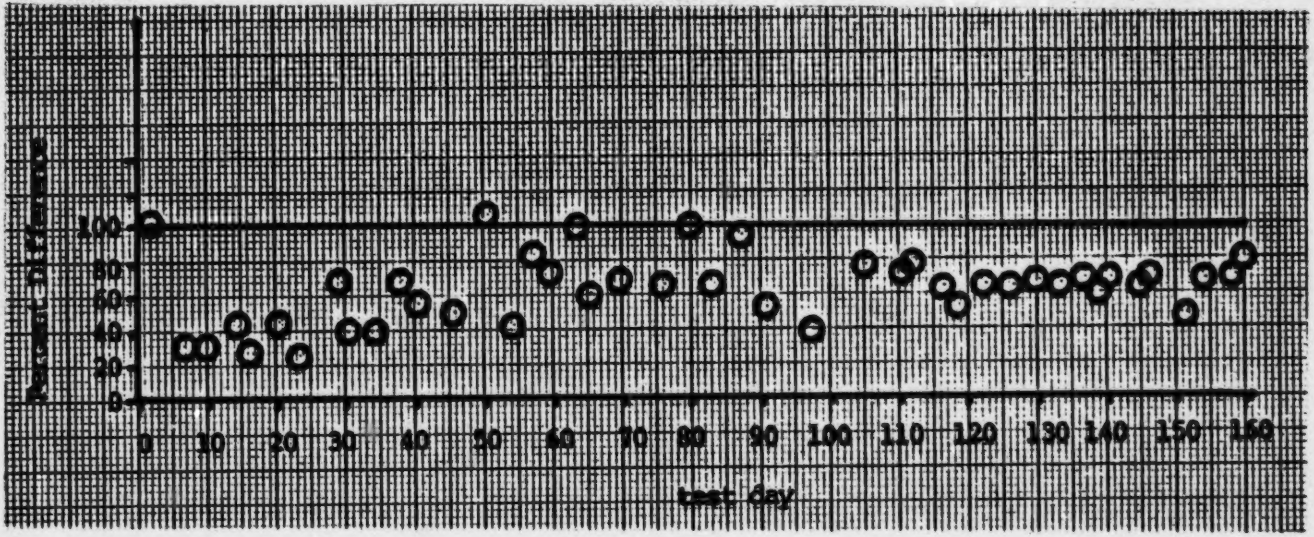


Figure 22. Percent difference of TOC levels of ozonated to nonozonated effluent from 10 ft. of BAC tower.

$$\frac{\text{THMFP effluent 2.5 ft. of ozonated BAC Tower}}{\text{THMFP effluent 2.5 ft. of nonozonated BAC Tower}} \times 100 = \begin{array}{l}\text{Percent difference of}\\ \text{ozonated BAC Tower effluent}\\ \text{compared to nonozonated}\\ \text{BAC Tower effluent}\end{array}$$

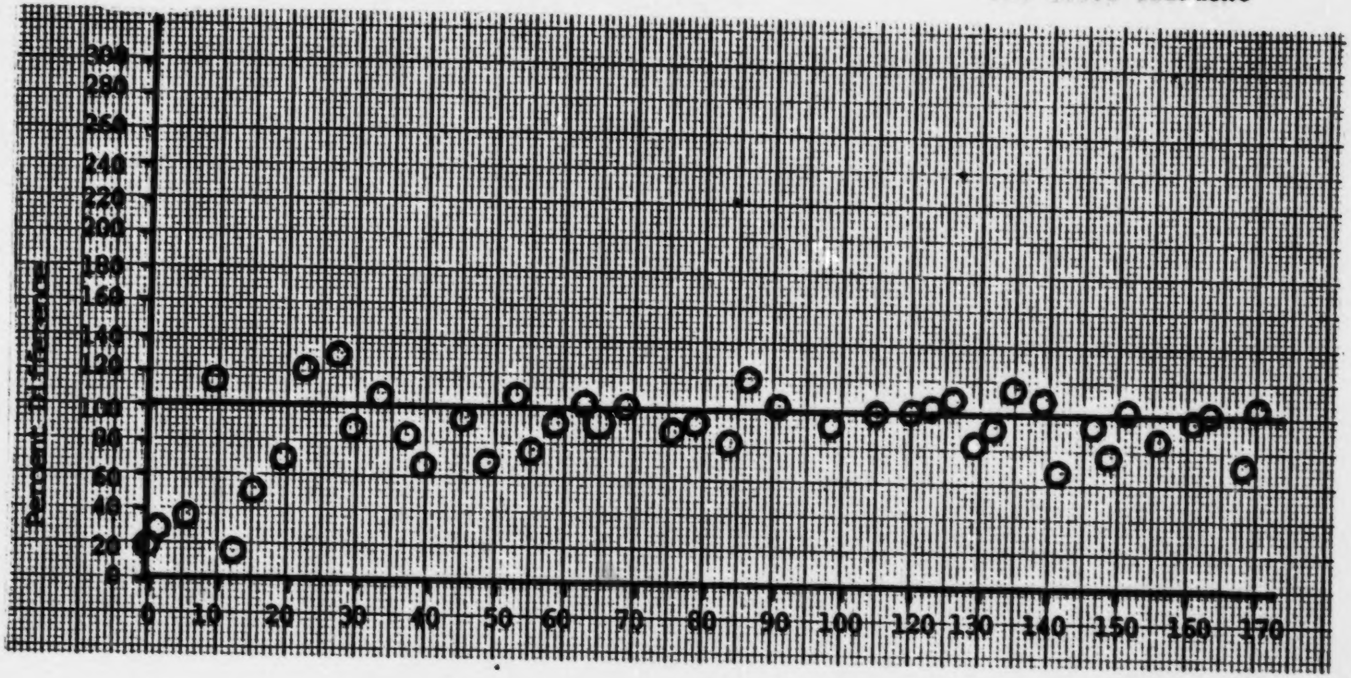


Figure 23. THMFP effluent from 2.5 ft. of bed depth of ozone-BAC tower compared with THMFP effluent from 2.5 ft. of bed depth of nonozone-BAC tower.

$$\frac{\text{THMFP effluent 5 ft. of ozonated BAC Tower}}{\text{THMFP effluent 5 ft. of nonozonated BAC Tower}} \times 100 = \text{Percent difference of ozonated BAC Tower compared to nonozonated BAC Tower}$$

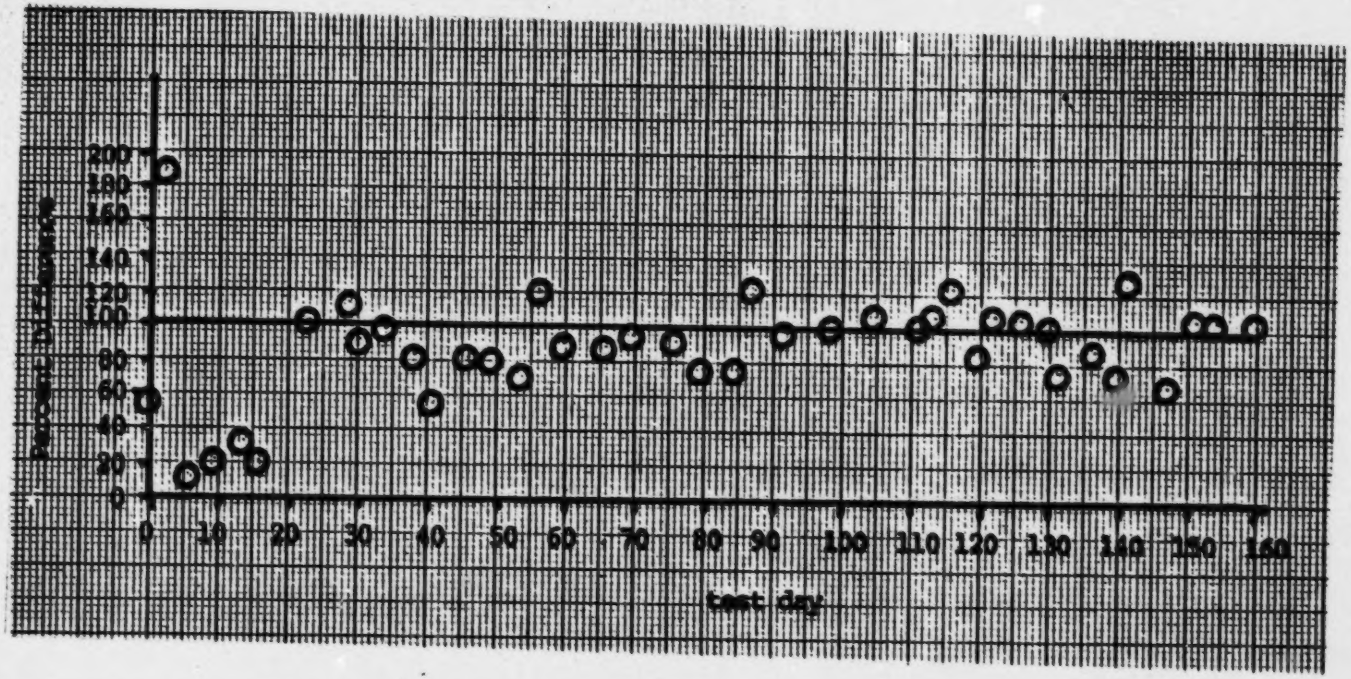


Figure 24. THMFP effluent from 5 ft. of ozone-BAC tower compared with THMFP effluent from 5 ft. of nonozone-BAC tower.

$$\frac{\text{THMFP effluent 10 ft. of ozonated BAC Tower}}{\text{THMFP effluent 10 ft. of nonozonated BAC Tower}} \times 100 = \text{Percent difference of ozonated BAC Tower compared to nonozonated BAC Tower}$$

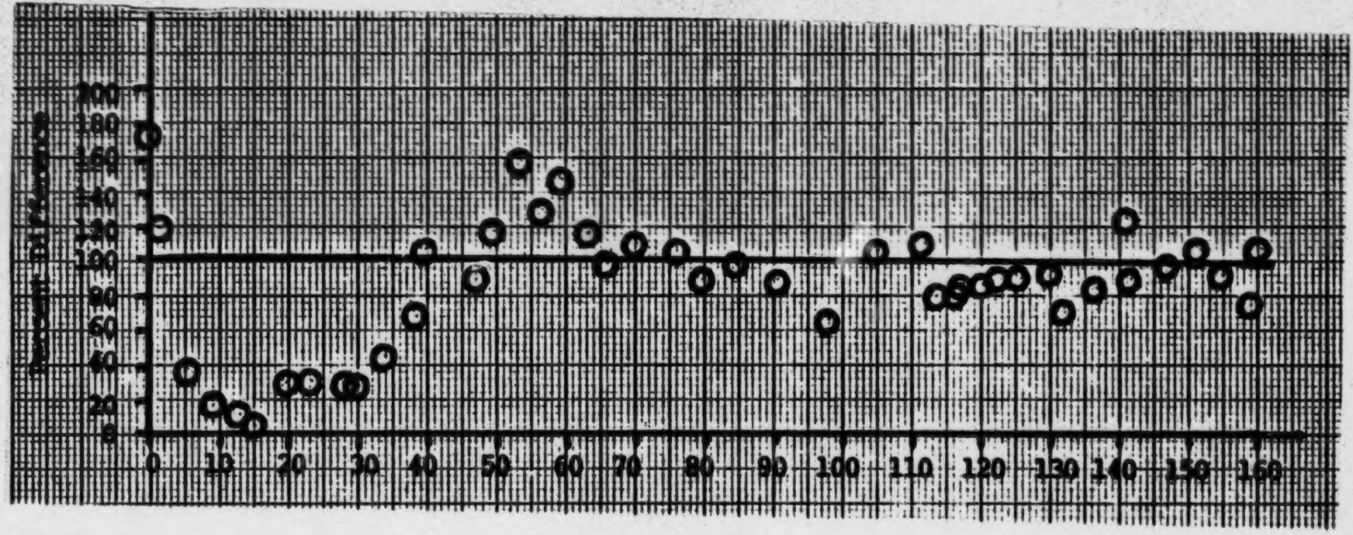


Figure 25. THMFP effluent from 10 ft. of ozone-BAC tower compared with THMFP effluent from 10 ft. of nonozone-BAC tower.

In Figures 23, 24 and 25, a similar comparison for THMFP shows that instead of a performance plateau region being reached, performance became essentially identical at approximately 10.5, 24.3 and 41.4 test days, respectively, for 2.5, 5 and 10 ft. of bed depth. The average THMFP passage from these test days was 98, 99 and 102 percent by ozone-BAC compared with the nonozone-BAC.

These TOC and THMFP comparisons are summarized in Table 10. If the two systems are rated based on these data, the conclusions would be as follows:

THMFP

The ozone-BAC system removed more THMFP than the nonozone-BAC system for 10.5, 24.3 and 41.4 days for bed depths of 2.5, 5 and 10 ft., respectively. After these periods, the performance of both systems was essentially identical.

TOC

The ozone-BAC system removed more TOC than the nonozone-BAC system for 21, 31 and 50 days with bed depths of 2.5, 5 and 10 ft., respectively. After these periods to the end of the testing period at 160 days, the ozone-BAC system allowed passage of 75, 72 and 72 percent as much TOC as the nonozone-BAC system for the 2.5, 5 and 10 ft. bed depth, respectively.

Turbidity—NTU

Average turbidity values for clearwell water and ozone contactor effluents were 0.4 and 0.22, respectively. The turbidity profiles through the towers at 2.5, 5 and 10 ft. depths for the ozonated, nonozonated, and sand tower were 0.16, 0.16, 0.16, 0.13, 0.17, and 0.25, 0.23 and 0.29, respectively.

Color—Units of Apparent Color

The color profile through the tower is shown in Table 1.

pH—

The average pH value of clearwell water and ozonated water was 8.5 and 8, respectively. The pH profile for the ozonated tower (2.5, 5 and 10 ft.) was 7.34, 7.29 and 7.25, a steady drop with bed depth. In the nonozonated tower, values were 8.61, 8.65 and 8.59, all up slightly from the pH 8 entering. Sand tower values were 8.57, 8.61 and 8.61, again up from the pH 8 entering.

Additional Analytical Data—

1) Other than the volatile halogenated organics, Preston raw and finished water and water in the pilot plant contained no organic EPA priority pollutants.

# TABLE 10

# PERFORMANCE COMPARISON OF OZONE-BAC VERSUS NONOZONE-BAC SYSTEMS

# BASED ON PLOTS IN FIGURES 118 THROUGH 123

## TOC COMPARISON

| Bed Depth | Ozone-Bac Performed Better Than Nonozone-BAC Systems as Follows, Based On Number Of Days To Reach A Plateau Region Of Performance | For Remaining Test Period, To 160 Days, The Plateau Performance Level Of The Ozone-BAC Was The Following Percentage Of The Nonozone-BAC System |
|---|---|---|
| 2.5 ft. | 21 days | 75 percent |
| 5 ft. | 31 days | 72 percent |
| 10 ft. | 50 days | day 50 to day 87 - 80 percent<br>average = 72%<br>day 87 to day 160 - 68 percent |

## THMFP COMPARISON

| Bed Depth | Ozone-BAC Performed Better Than Nonozone-BAC Systems As Follows, Based On Number Of Days To Reach A Region Of Identical Performance | For Remaining Test Period, To 160 Days, The Level Of Ozone-BAC Performance Was The Following Percentage Of The Nonozone-BAC System Performance |
|---|---|---|
| 2.5 ft. | 10.5 days | 98 |
| 5 ft. | 24.3 days | 99 |
| 10 ft. | 41.4 days | 102 |

2) From initial startup, and throughout the entire test period, no PAH's were eluted from the virgin GAC.

Summary of Results for Chemical Parameters

1) Over the full test period, the average absorbed ozone dose was 11.3 mg/L (43 mg/gal). The average TOC and THMFP of the water being ozonated was 7.7 mg/L and 438 µg/L, respectively. After an ozone contact time totaling approximately 11 minutes (an overall transfer efficiency of 74 percent through an MOC and a BOC in series), the average level of free ozone was 0.02 mg/L.

2) Over the full test period, ozonation alone resulted in a 13-percent TOC reduction (7.7 mg/L entering and 6.7 mg/L in the effluent). There was a 7-percent increase in the THMFP level (438 µg/L entering and 467 µg/L in the effluent), but this difference may not be significant).

3) The effective bed life of a BAT on our system as studied can be determined based on several criteria. We present two criteria, the first of which is the better (if removal of THMFP is the primary concern) because of subsequent THM growth following breakpoint chlorination. Criterion 1 is based on bed-life criteria developed in our previous work (Ref. 6)—that is, when 3 mg/L of TOC or 200 µg/L of THMFP breakthrough occurs, subsequent chlorination to 2.5 ppm of free chlorine (1 hr of chlorine contact time) results in a THM growth of 100 µg/L (after aging 2 days or until all free chlorine is gone). Criterion 2 is based on run days to reach saturation (effluent of TOC and THMFP equal influent). Both are expressed in Tables 8 and 9.

Thus ozone treatment extended the Criterion 1 bed life by a factor of 2.2, and the Criterion 2 bed life by a factor of 1.5. In the next research phase, the BAC tower will be operated aerobically from the beginning.

4) Ozone is very effective in removing one and two chlorine chloroethylenes and chlorinated benzenes.

5) From initial startup and throughout the entire test period, no PAH's were eluted from the virgin GAC.

6) On our water, ozone (11.3 mg/L) was at least as effective as breakpoint chlorination (18 mg/L) in color removal.

## RESULTS FOR BACTERIOLOGICAL PARAMETERS STUDIED

The purpose of this phase of the work was to determine whether or not ozonating water resulted in a change in naturally occurring THM precursors to favorably increase the removal of the altered substances by a BAC tower and thus increase GAC bed life.

Samples for bacteriological analyses were taken weekly. The mean, standard deviation, and range of the total plate counts/mL obtained are given in Table 11. Raw water counts for the period were somewhat greater than those found at the Preston plant during previous experiments. The Medley Well Field was drawn from during this time and may have caused this increase. The Hialeah Well Field yielded similar values during the same seasons last year,

## TABLE 11

## MEAN, STANDARD DEVIATION AND RANGE OF PLATE COUNTS/ML IN PILOT PLANT SAMPLES (11 WEEKLY SAMPLES)

| SAMPLE | | $\bar{X}$ | S.D. | RANGE |
|---|---|---|---|---|
| | | **SUPPLY** | | |
| 1 | Raw | 1,000 | 1,100 | 0 - 3,500 |
| 1 | L.S. | 330 | 330 | 1 - 1,000 |
| 2 | P (Preston) | 11 | 13 | |
| 2 - 1 | | 1 | 1 | 0 - 48 |
| 2 | P (Preston) | 1 | 1 | 0 - 2 |
| 3 | Clear well | 3,700 | 4,000 | 0 - 14,000 |
| 7 | BOC | 1,300 | 2,200 | 0 - 7,800 |
| | | **EFFLUENTS** | | |
| GAC/0 | A8-1,2.5 | 220,000 | 310,000 | 1,200 -1,000,000 |
| | A8-4,10.0 | 280,000 | 320,000 | 0 - 990,000 |
| Sand | C8-1,2.5 | 30,000 | 42,000 | 300 - 150,000 |
| | C8-4,10.0 | 100,000 | 250,000 | 700 - 840,000 |
| GAC | D8-1,2.5 | 18,000 | 20,000 | 300 - 77,000 |
| | D8-4,10.0 | 28,000 | 45,000 | 490 - 160,000 |

(Continued)

## TABLE 11 (CONTINUED)

| SAMPLE | $\bar{X}$ | S.D. | RANGE |
|---|---|---|---|
| | **CHLORINATED EFFLUENTS, UNAGED** | | |
| A-9 GAC/0 | 44 | 120 | 0 - 420 |
| C-9 Sand | 600 | 1,900 | 0 - 6,000 |
| D-9 GAC | 1 | 2 | 0 - 300 |
| | **CHLORINATED EFFLUENTS AGED 2 DAYS** | | |
| A-9+2 GAC/0 | 140 | 430 | 0 - 1,300 |
| C-9+2 Sand | 24 | 49 | 0 - 150 |
| D-9+2 GAC | 53 | 160 | 0 - 510 |
| | **CHLORINATED EFFLUENTS, AGED 6 DAYS** | | |
| A-9+6 GAC/0 | 0* | | 0 - 30,000 |
| C-9+6 Sand | >1 | 1 | 0 - >3,000 |
| D-9+6 GAC | 86 | 260 | 0 - >3,000 |

* Counts that exceeded dilution limits (30-300 colonies per plate) were not included in calculating mean.

thus these higher counts from the raw water may reflect normal annual fluctuations. No indicator organisms or pathogens were detected in raw or treated water samples.

Bacterial counts were high from the beginning of the experiment on day 0 in all samples (e.g., 3500/mL in raw water and 880 in the clear well), which would have effectively inoculated subsequent components of the system. The BOC chamber samples yielded counts above 500/mL on all except four sample dates. Occasional samples taken from the MOC chamber yielded no bacterial growth. Apparently bacteria survived ozonation and regrowth occurred in the TOC. Oxygen concentrations up to 7 mg/L, turbulence, and residual organic solutes may favor growth there in spite of the presence of ozone.

Counts/mL obtained from the GAC-ozone tower (A-series) were consistently greater than those from the GAC without ozone (D-series) after 7 days of operation. Generally, the bacterial count/mL of effluent samples from the BAC-ozone tower were 10 times greater than those from the GAC tower effluents. These values resembled those obtained in earlier work with bench-scale carbon columns, whereas the values obtained from GAC without ozone were much lower. The GAC tower effluent counts were one-tenth those obtained from GAC columns in bench-scale experiments. Sand tower values were similar to sand column values, but they exhibited greater variation with depth of the sand than did previously reported sand column values.

On several sample days, counts of 1/mL were obtained from effluents chlorinated to 2 ppm. Counts greater than 1/mL were obtained from these samples aged for 2 days when the concentration of free residual chlorine was either 0 or very low.

The population composition was similar in all samples taken from the entire system. More population uniformity between different components of the system was seen than in bench-scale experiments. Table 12 is a list of the frequency of occurrence of all identified organisms in each sample. *Alcaligenes* spp. and pseudomonads occurred most frequently in raw water and in subsequent treatment steps through the BOC, but other species also were isolated more frequently in tower effluent samples than in raw water, lime softener, or clearwell samples. The GAC effluents at each level of the tower seemed to have the greatest diversity of species (Table 12).

Gram-negative rods in low numbers survived chlorination to 2 ppm in tower effluents and occasionally increased in numbers after 2 days of aging as residual free chlorine dissipated. A-9 (GAC-ozone) had *Acinetobacter* spp., *Moraxella* spp., pseudomonads, and unidentified species at least one time out of the 11 sample dates. Sand tower effluent yielded unidentified species on three sample dates, and GAC effluent did so four times. After 2 days of aging, *Moraxella* spp. were recovered twice from samples of effluent from the GAC-ozone tower, and pseudomonads were recovered once. Unidentified species only were isolated from 6 days of aged GAC-ozone effluent. Chlorinated sand tower effluent aged for 2 days yielded Gram-positive cocci and pseudomonads once in addition to the occurrence of unidentified species found in the unaged sample. Only unidentified species were recovered from 6-day-old chlorinated sand tower effluent.

## TABLE 12

## FREQUENCY OF OCCURRENCE OF ORGANISMS
## (PERCENT OF POSSIBLE TIMES ORGANISM OCCURRED, 11 SAMPLE DATES)

| Organism | Raw | LS | CW | BOC | GAC-Ozone | | | Sand | | | GAC | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 7 | A 8-1 | A 8-4 | A-9 | C 8-1 | C 8-4 | C-9 | D 8-1 | D 8-4 | D-9 |
| Alcaligenes spp. | 54 | 64 | 45 | 45 | 27 | 27 | | 27 | 27 | | 18 | 36 | |
| Acinetobacter spp. | 9 | 45 | 27 | 18 | 27 | 27 | 18 | 18 | 23 | | 45 | 27 | |
| Gram + Rods<br>Gram + Cocci | 9 | 9 | 9 | 27 | 9 | 18 | | 18 | 18 | 18 | 36 | | |
| Moraxella spp. | 36 | 18 | 18 | 27 | 36 | 27 | 9 | 27 | 45 | | 45 | 45 | |
| Pseudomonas spp. | 31 | 36 | 9 | 18 | 18 | 27 | | 27 | 27 | | 27 | 27 | |
| pseudomonads | 45 | 73 | 36 | 45 | 45 | 45 | 9 | 36 | 54 | | 64 | 54 | |
| Unidentified | 18 | 18 | 27 | 45 | 36 | 18 | 27 | 36 | 27 | 27 | 27 | 45 | 36 |
| CDC Grps. | 9 | 9 | 18 | 9 | 18 | 18 | | | 9 | 45 | 9 | 9 | |

(Continued)

## TABLE 12 (CONTINUED)

## FREQUENCY OF OCCURRENCE OF ORGANISMS IN CHLORINATED, AGED EFFLUENT SAMPLES (PERCENT OF TIMES ORGANISM OCCURRED, 11 SAMPLE DATES)

SAMPLE

| Organism | GAC-Ozone | | | Sand | | | GAC | | |
|---|---|---|---|---|---|---|---|---|---|
| | A 9+0 | A 9+2 | A 9+6 | C 9+0 | C 9+2 | C 9+6 | D 9+0 | D 9+2 | D 9+6 |
| *Acinetobacter* spp. | 18 | | | | | | | | 9 |
| Gram + Cocci | | | | | 9 | | | | 9 |
| *Moraxella* spp. | 9 | 18 | | | | | | | |
| pseudomonads | 9 | 9 | | | 18 | | | | 9 |
| Unidentified spp. | 27 | 9 | 18 | 27 | 9 | 9 | 36 | 64 | 9 |
| CDC Groups | | | | 45 | | | | | |

The GAC tower (D) effluent samples yielded unidentified species at all ages. In addition *Acinetobacter* spp., Gram-positive cocci, and pseudomonads were observed. Most of the organisms were Gram-negative rods and were expected to be susceptible to disinfection. Their occurrences usually coincided with absence or very low concentrations of residual free chlorine. All of the unidentified species were Gram-negative rods that occurred in low counts/mL and almost exclusively when residual chlorine was absent.

On any sample day, the dominant organism in an early step of the process could be traced through the entire system. For example, on the startup day, *Moraxella* spp. and Gram-positive rods were recovered throughout the system. As other bacteria entered and established colonies, they could be traced through the system. After 6 weeks of operation, CDC Group II F became dominant through the system, replacing *Alcaligenes* spp., which previously had gone through and was in turn replaced the next week by pseudomonads.

Results of culturing sonicated carbon granules and sand from the towers are shown in Table 13. The duplicate sand values agree, probably because sand may not trap bacteria as readily as GAC and the bacteria may become more uniformly distributed by the water flow. The carbon values are greatly different because bacteria were not uniformly distributed on the carbon surface.

## TABLE 13

## PLATE COUNTS/ML OBTAINED FROM CARBON GRANULES AND SAND

| Source | Sonicated 4 Min - 20 KHZ Replicate Plates Made On R2A | | | |
|---|---|---|---|---|
| | Number Of Colonies/ML | | | |
| | Top | Top Ave. | Bottom | Bottom Ave. |
| TOWER A | | | | |
| GAC & 03 | 400,000 | 340,000 | 520,000 | 450,000 |
| | 270,000 | | 380,000 | |
| TOWER D | | | | |
| GAC, no 03 | 590,000 | 430,000 | 200,000 | 380,000 |
| | 260,000 | | 500,000 | |
| TOWER C | | | | |
| Sand, no 03 | 91,000 | 100,000 | 56,000 | 48,000 |
| | 117,000 | | 40,000 | |

# SECTION 6

## PILOT PLANT STUDY NO. 2: EFFECTS OF OZONATED INFLUENT ON THMFP WITH AN AEROBIC BAC SYSTEM

Pilot Plant Study No. 2 (PS 2), like PS 1, was designed to study the performance of an ozone-BAC tower system compared with a nonozone-BAC tower system, but under aerobic BAC tower conditions from initial startup. Oxygen was added to both BAC towers during the entire 172-day testing period.

## PILOT PLANT MODIFICATIONS

Pilot Plant Sections I and II remained as described in Section 4 (see Figures 1 and 2). A flow diagram for Section III is shown in Figure 26. As in PS 1, the water flow rate was 3 gpm/ft$^2$ through both BAC towers.

BAT C (Figure 26) received ozonated water, and BAT D received nonozonated water. After each tower, the water was chlorinated before entering the chlorine contact basin that followed each tower. The level of chlorination was adjusted to provide a 2.5-ppm free chlorine residual after a contact time of 1 hour. Filtrasorb F-400 was used in both towers and was taken from the same manufactured lot as used in PS 1. The quantity of oxygen added was adjusted by gas flow meters at each sampling port to assure a DO level of approximately 6 ppm in the 10-ft. effluent sample water (the oxygen influent was turned off when sampling was done).

## RESULTS FOR CHEMICAL PARAMETERS STUDIED

### Pilot Plant Section I Chemical Data

#### Dissolved Oxygen—

The level of dissolved oxygen at all the sampling points in all three pilot plant sections is shown in Table 14.

The DO level in raw water from the wells was always zero. For part of PS 1, air was bubbled into one or more of the chlorine contact basins and the clearwell to try to raise the DO level to a value that would result in an average DO level of 6 ppm or above in the nonozone-BAC tower. This was never possible, so in PS 2, oxygen was added to both BAC towers from initial startup. In PS 1, even the ozone contact effluent with an average DO level above 7 ppm would not maintain a high enough DO level in the ozone-BAC tower effluent.

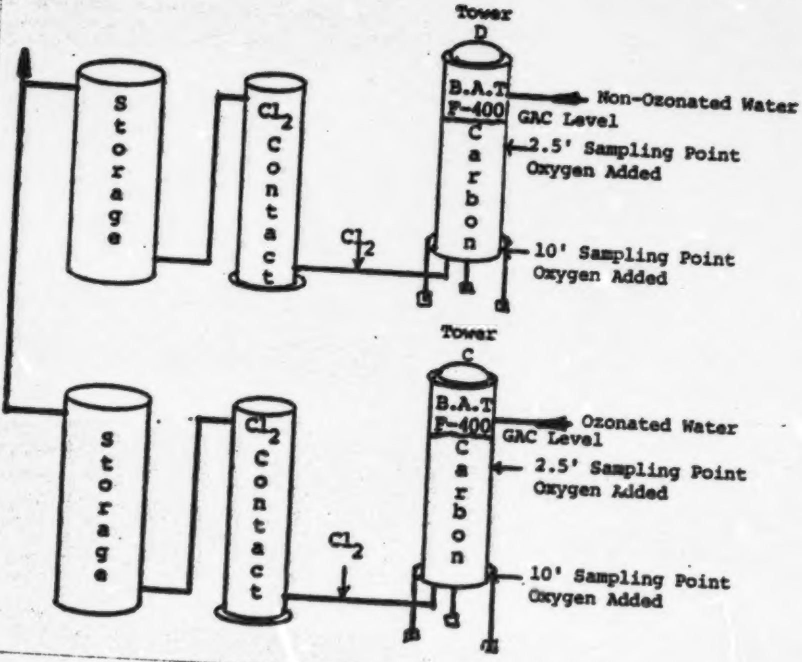

Tower D
B.A.T
F-400
Non-Ozonated Water
GAC Level
Carbon
2.5' Sampling Point
Oxygen Added
10' Sampling Point
Oxygen Added
Storage
Cl2 Contact
Cl2
Tower C
B.A.T
F-400
Ozonated Water
GAC Level
Carbon
2.5' Sampling Point
Oxygen Added
10' Sampling Point
Oxygen Added
Storage
Cl2 Contact
Cl2

Figure 26. Section III of pilot plant: BAT's, chlorine contact basin, and storage.

## TABLE 14

## DISSOLVED OXYGEN PROFILE FOR PS 2

| | | | | | Average DO, ppm |
|---|---|---|---|---|---|
| Raw Water | | | | | 0.0 |
| Lime-Softened Water | | | | | 0.15 |
| Clearwell effluent (after recarbonation) | | | | | 0.6 |
| MOC & BOC effluent | | | | | 6.8 |
| Nonozone-BAC Tower | Test Period | | | | |
| | Day 0 | Day 1.6 | Day 2.6 | Day 3.6 To 6.6 | Day 6.6 To 172 |
| 2.5 ft. | nil | nil | 11.4 | 12 | average 12 |
| 5 ft. | nil | nil | >15 | 12 | average 12 |
| 10 ft. | 0.1 | 2 | 1.3 | 12 | average 6 |
| Ozone-BAC Tower | | | | | |
| 2.5 ft. | 0 | nil | 10.8 | >15 | average 12 |
| 5 ft. | nil | nil | 8.4 | >15 | average 12 |
| 10 ft. | 0.4 | 4.3 | 5.6 | 12.2 | average 6 |

### Turbidity—NTU

The turbidity profile is shown in Table 15. Throughout the test period, the raw water turbidity average was 0.47. Turbidity out of the lime-softener averaged 7.2. After recarbonation and sand filtration the average value was 0.23 in the clearwell.

### Color—Units of Apparent Color

The color profile is shown in Table 16. Lime-softening reduced the raw water color from 25 to 13. The clearwell effluent had an average color of 10. Ozonation reduced the clearwell effluent water to a value of 2.

## TABLE 15

## AVERAGE TURBIDITY PROFILE VALUES FOR SECOND OZONE-BAC STUDY (PS 2)

| | AVERAGE TURBIDITY UNITS, NTU | |
|---|---|---|
| Raw Water | 0.47 | |
| Lime-Softener Effluent | 7.2 | |
| Clearwell Effluent | 0.23 | |
| MOC & BOC Effluent | 0.16 | |
| | D-Tower, Nonozonated Water | C-Tower Ozonated Water |
| 2.5 ft. | 0.25 | 0.21 |
| 5 ft. | 0.24 | 0.17 |
| 10 ft. | 0.23 | 0.2 |

## TABLE 16

## AVERAGE COLOR PROFILE VALUES FOR SECOND OZONE-BAC STUDY (PS 2)

| | AVERAGE COLOR UNITS, Apparent Color | |
|---|---|---|
| Raw Water | 25 | |
| Lime-Softener Effluent | 13 | |
| Clearwell Effluent | 10 | |
| MOC & BOC Effluent | 2 | |
| | D-Tower, Nonozonated Water | C-Tower Ozonated Water |
| 2.5 ft. | 7 | 2 |
| 5 ft. | 6 | 1.7 |
| 10 ft. | 5 | 1.5 |

### pH—

The pH profile is shown in Table 17. Lime-softening raised the pH of raw water from 7.1 to 9.9. The average pH of the clearwell effluent, after recarbonation, was 8.4.

TABLE 17

AVERAGE PH PROFILE VALUES FOR SECOND OZONE-BAC STUDY (PS 2)

| | AVERAGE pH | |
|---|---|---|
| Raw Water | 7.1 | |
| Lime-Softener Effluent | 9.9 | |
| Clearwell Effluent | 8.4 | |
| MOC & BOC Effluent | 8.0 | |
| | D-Tower, Nonozonated Water | C-Tower, Ozonated Water |
| 2.5 ft. | 8.23 | 7.35 |
| 5 ft. | 8.1 | 7.22 |
| 10 ft. | 8.12 | 7.11 |

### Halogentated Organics—

The halogenated organic profile is shown in Table 18.

TABLE 18

AVERAGE CONCENTRATION (μg/L) OF HALOGENATED ORGANICS FOR SECOND OZONE-BAC STUDY (PS 2)

| COMPOUNDS | Raw Water | Lime-Softened Water | Clearwell Water | MOC & BOC Effluent | % Reduction |
|---|---|---|---|---|---|
| Vinyl Chloride | 9.8 | 8.3 | 6.5 | 0.6 | 91 |
| Trans 1,2-Dichloroethene | 0.9 | 0.95 | 0.93 | 0.07 | 92 |
| 1,1-Dichloroethane | 2.8 | 2.8 | 2.8 | 2.7 | 4 |
| Cis 1,2-Dichlorethene | 27.1 | 28.2 | 24 | 2.5 | 90 |
| Trichloroethylene | 0.8 | 0.8 | 0.7 | 0.2 | 71 |
| Tetrachloroethylene | Values too low to report | | | | |
| Chlorobenzene | 1.0 | 0.9 | 0.9 | 0.05 | 94 |
| p-Chlorotoluene | 0.26 | 0.35 | 0.27 | 0.027 | 90 |
| m-Dichlorobenzene | Values too low to report | | | | |
| p-Dichlorobenzene | 0.26 | 0.32 | 0.27 | 0.017 | 94 |
| o-Dichlorobenzene | 0.36 | 0.4 | 0.3 | 0.03 | 90 |

THM—

In PS 2, consisting of 172 days of operation and 50 sampling days, the instantaneous THM raw data tables showed that small amounts of THM's occasionally appeared in the raw water feed to the pilot plant. As explained in Section 5, this was due to the location of our raw water feed line close to one of the lime softeners at the Preston plant. At the Preston plant, chlorine was added to sodium silicate to form colloidal silica as a flocculation aid in the lime softener, resulting in the formation of THM's in the Hydrotreator. Whenever the Hydrotreator was shut down, it was possible for a small amount of the water in the Hydrotreater to move backwards into the raw water feed line because the pilot plant continued to operate. It would have been very costly to relocate the pilot plant raw water feed line, and the amount of THM involved was not detrimental to our study.

Vinyl Chloride—

From Table 18, we observe that the average levels of vinyl chloride in the raw water, lime-softener effluent, and clearwell effluent after recarbonation were 9.8, 8.3 and 6.5 μg/L, respectively.

Trans 1,2-Dichloroethene—

The average values at the three sampling points were 0.9, 0.95 and 0.93 μg/L, respectively. The high and low values were 5.9 μg/L and nil.

1,1-Dichloroethane—

The average value at all three sampling points was 2.8 μg/L, with high and low values of 11.1 μg/L and 0.07 μg/L.

cis 1,2-Dichloroethene—

The average values at all three sampling points were 27.1, 28.2 and 24 μg/L, respectively, with high and low values of 68.4 and 0.8 μg/L.

Trichloroethylene—

The average values at all three sampling points were 0.8, 0.8 and 0.7 μg/L, with high and low values of 2.7 μg/L and nil.

Tetrachloroethylene—

Values were too low to report (below normal detection limit). This was also true for m-dichlorobenzene.

Chlorobenzene—

The average values at all three sampling points were 1.0, 0.9 and 0.9 μg/L, with high and low values of 3.6 μg/L and nil.

p-Chlorotoluene—

The average values at all three sampling points were 0.26, 0.35 and 0.27 µg/L, with high and low values of 2.2 µg/L and nil.

p-Dichlorobenzene—

The average values at all three sampling points were 0.26, 0.32 and 0.27 µg/L, with high and low values of 2.1 µg/L and nil.

o-Dichlorobenzene—

The average values at all three sampling points were 0.36, 0.4 and 0.3 µg/L, with high and low values of 1.3 µg/L and nil.

TOC—

TOC profile data for Section I of the pilot plant are graphed in Figures 27 and 28. Figure 27 shows that the TOC level in the raw water from initial startup (0.6 days of sampling time) to a sampling time of 7.6 days was much higher than for the remaining testing period. The average TOC influent to test day 7.6 was 14.2 ppm, and for the remaining of the test period it was 9.3 ppm. This pattern was reflected in the lime-softener and clearwell effluents. The lime-softener effluent averaged 11.2 ppm for the first 0.6 days and 6.97 ppm for the remainder of the testing period. Respective values for the clearwell effluent after recarbonation were 10.7 and 6.77 ppm.

For the first 7.6 days, the lime-softener removed 21% of the influent TOC, and the value out of the clearwell was 25% of the raw water influent. For the remainder of the testing period, the lime softener removed an average of 25% from the influent water, and the clearwell effluent level was 28% of the raw water influent. These removal values compare closely with our previous experience in this study.

THMFP—

THMFP profile data are graphed in Figures 29 and 30. Raw and lime-softened results are plotted in Figure 29. It is apparent that over the 172-day testing period, the THMFP level in raw water varied, perhaps more so than the TOC level (Figure 27). In Figure 29, we can consider the raw water data in two sections—day 0 to day 65 (May 5, 1981, to July 10, 1981) and day 65 to day 172 (July 10, 1981, to November 6, 1981). In the first section, the raw water shows two very high data points, test day 3.6 and 7.6. These appear to be real values. Our pilot plant was operated as a regular plant, with all the associated problems, and high values for THMFP occurred. Possible reasons for occasional high values will be discussed later in this report. In the first 65-day test period, THMFP values appear to average higher than the remainder of the test period. The average value was 886 µg/L from day 0 to 65 and 392 µg/L for the remainder of the test period. Corresponding values for lime-softened water were 613 µg/L and 290 µg/L, respectively. Thus lime softening removed 31% and 26%, respectively, for the two time periods.

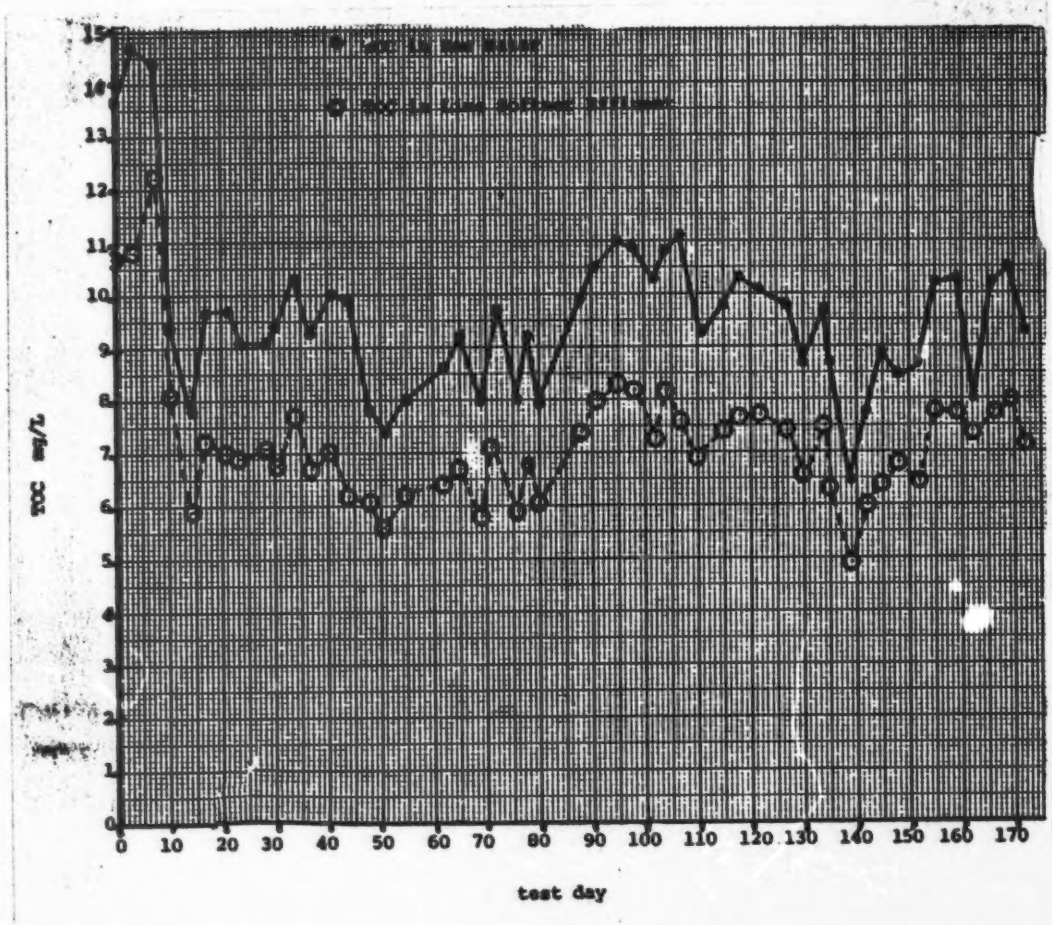


Figure 27. TOC profile of raw water and effluent from lime softener.

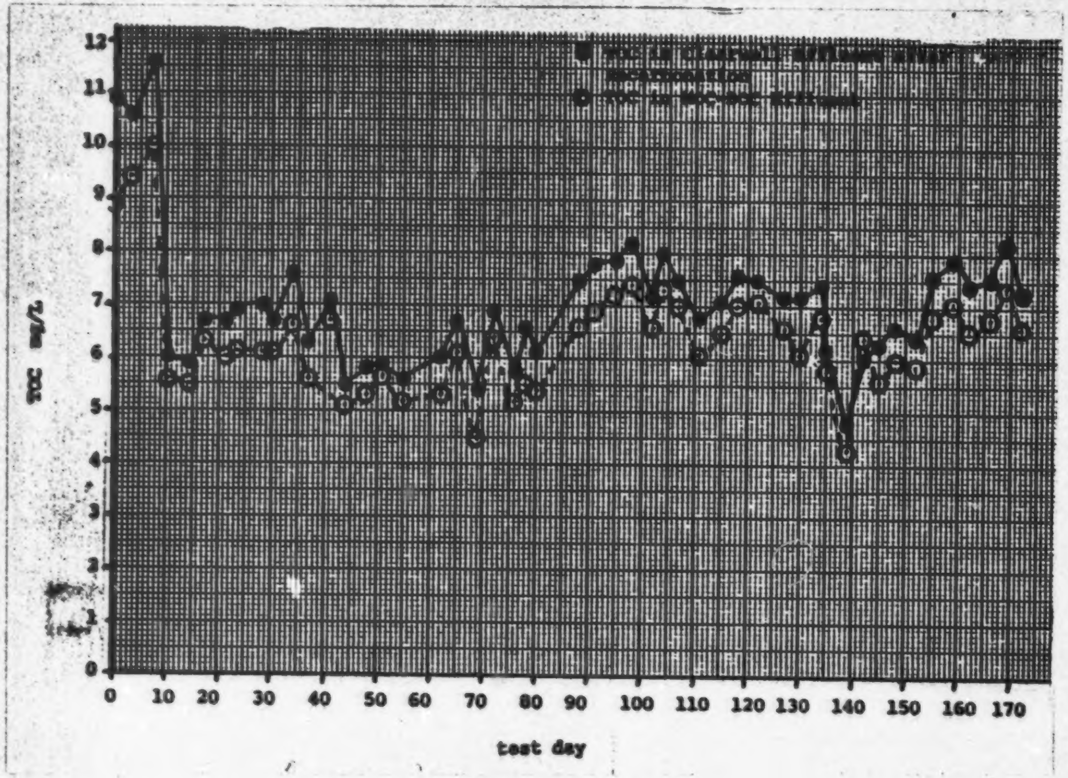


Figure 28. TOC profile of clearwell effluent after recarbonation and TOC effluent from MOC-BOC.

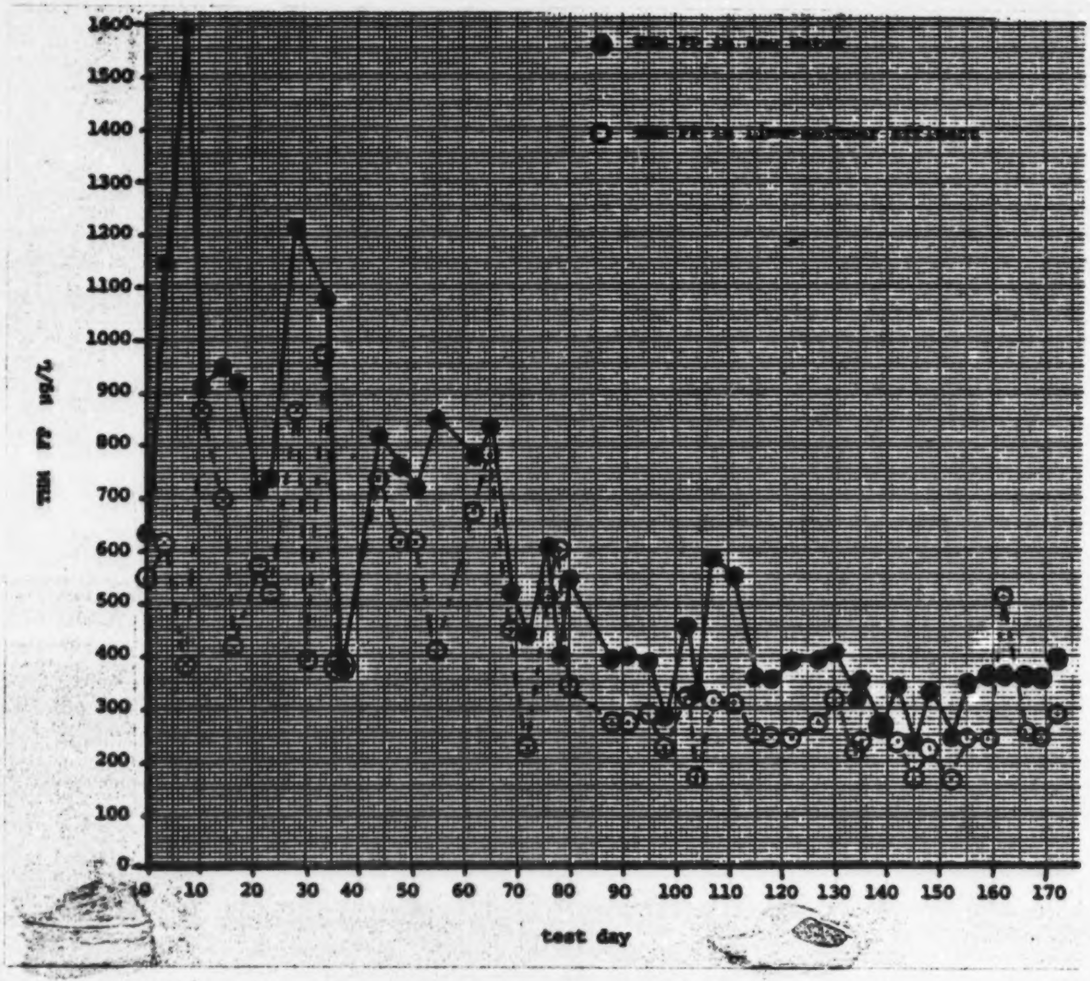


Figure 29. THMFP profile for raw water and lime-softener effluent.

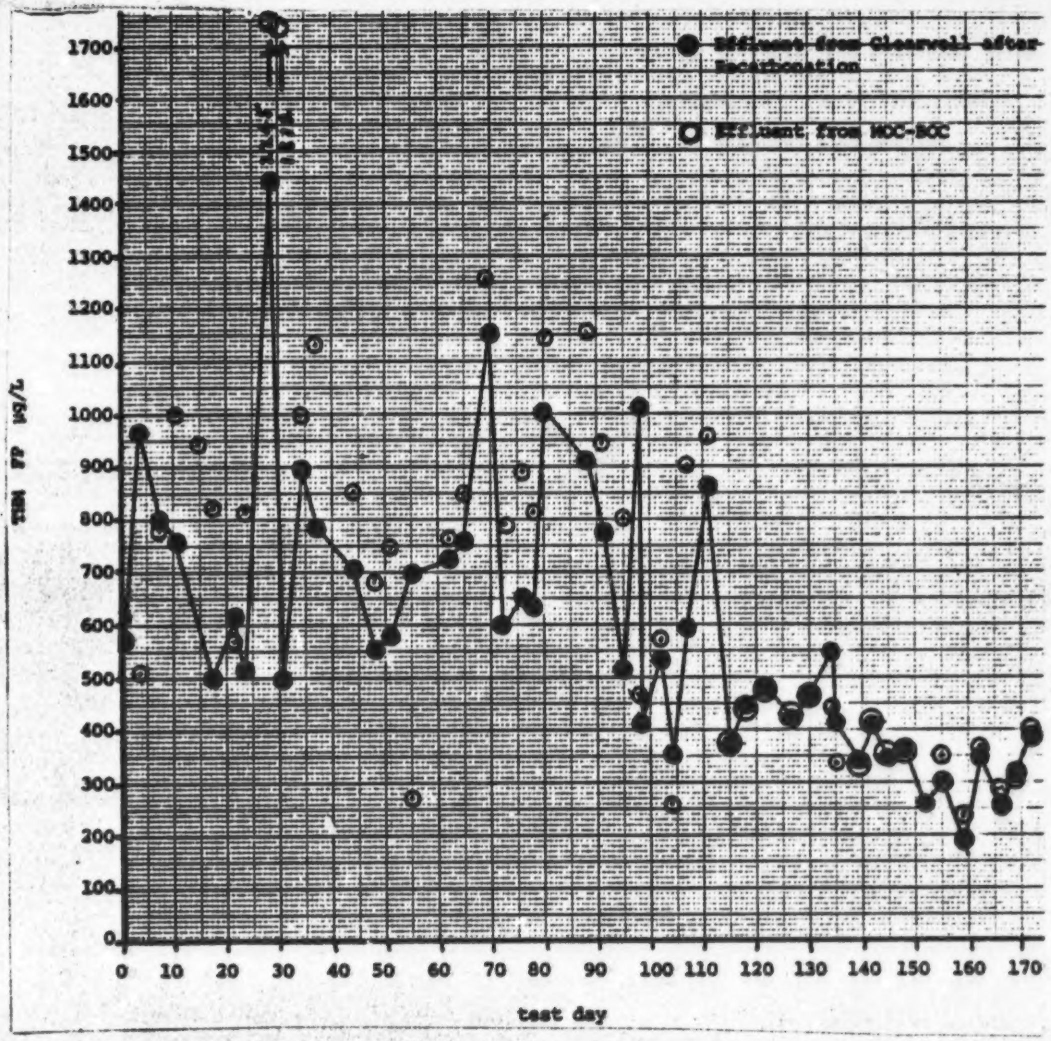


Figure 30. THMFP profile data in clearwell effluent after recarbonation and MOC-BOC effluent.

The average THMFP values for the clearwell effluent- recarbonation sample point (before the water entered the ozone contactor) are plotted in Figure 35. These data can once again be considered in two sections, an average for the first 65 test days and an average for the remaining of the 172-test-day period. Table 19 compares the two sections.

### TABLE 19

### AVERAGE THMFP VALUES IN PILOT PLANT SECTION I (PS 2)

| Sample Point | Average First 65 Test Days | Average Remaining 107 Test Days |
|---|---|---|
| Raw Water | 886 | 392 |
| Lime-Softened | 613 | 290 |
| Clearwell Recarbonation | 725 | 518 |

Note that in the first 65 test days, the average concentration of THMFP in the clearwell-recarbonation sample was 118 percent higher than the lime-softened water. In the remaining 107-test-day period, the THMFP average increase was 179 percent. In both sections, a substantial increase was observed. We will show in the discussion in the next section of this paper (pilot plant Section II) that this increase is a result of oxygen in the air reacting with TOC in the groundwater forming additional THMFP. The oxygen picked up by contact with air in the chlorine contact basins, sand filter, and clearwell was apparently still enough to allow conversion of some TOC to THMFP.

Occasionally in the 172-day-test period, we experienced very high levels of THMFP in some water samples. These data points were carefully rechecked with the same high values obtained, values over one or two thousand µg/L. We now believe that such values are most likely real. Occasionally our pilot plant was shut down for periods of one or more days. Water would remain in the open lime softener, chlorine contact basins and clearwell, exposed to the air. At the time we did not actually sample such standing water for an increase in THMFP level. This should be done at some time in the future. We have noted in the past that surface waters in Florida in the same area always have a much higher THMFP level than the groundwaters, which have not always coincided with higher TOC values. Perhaps this is due to reaction with oxygen in the air. In the preceding discussion on TOC, we did not see a corresponding increase in TOC levels between the lime-softened and clearwell recarbonation sample points. We actually saw a small decrease.

## Pilot Plant Section II Results

Dissolved Oxygen—

The average level of DO entering the ozone contactors was 0.6 ppm and the effluent level in the MOC-BOC series ozone contactors was 6.8 ppm (Table 13).

Adsorbed Ozone Dose—

The Kerag RB 90/200 MOC provided an ozone transfer efficiency of 55 percent. Contact time in the MOC was 2.8 minutes. The ozone content of the MOC effluent averaged 0.54 mg/L. When an effluent sample was taken and held 2.2 minutes before ozone analysis, representing a total contact time of 5 minutes, the free ozone level was always zero. The ozone demand for our water was so high that to achieve the absorbed ozone dose level desired, we had to improve the transfer efficiency in order to adequately treat 25 gpm. To accomplish this, the stainless steel tank following the MOC, which was originally designed as an additional contact time reservoir for the MOC, was converted to a BOC, as described earlier. Retention time in the BOC was approximately 11.3 minutes. The overall transfer efficiency of the MOC-BOC series was 77 percent. Effluent water from the BOC averaged 0.00 mg/L of free ozone. Over the test period, the absorbed ozone dose averaged 14.5 mg/L (54.9 mg/gal).

Turbidity—

The average turbidity of the water entering and leaving the MOC-BOC series contactors was 0.23 and 0.16, respectively (Table 15).

Color—

The average color of the water entering and leaving the MOC-BOC series contactors was 10 and 2, respectively (Table 16).

pH—

The average pH of the water entering and leaving the MOC- BOC series contactors was 8.4 and 8.0, respectively (Table 17).

Halogenated Organics—

The halogenated organic profile of the water entering and leaving the MOC-BOC series contactors is shown in Table 18. The percent change for each compound is also shown. As in PS 2, note that double-bond halogenated organics all show marked reduction. The effect of reduction in concentration by aeration is very small. In Table 18, note again (as in PS 1) the concentration of 1,1-dichloroethane was only slightly reduced (4%).

To confirm the reduction of certain organics (double-bond halogenated) by ozonation, a separate experiment was set up. Over a 3-day period, organics were measured in and out of the MOC-BOC series contactor, 8 sample points each with ozone and air, and with air alone. This was accomplished by passing the normal amount of air through the ozone generator with and without the voltage on. The results are shown in Table 20.

## TABLE 20

## EFFECT OF OZONE + AIR AND AIR ALONE ON ORGANIC SUBSTANCES IN AND OUT OF THE MOC-BOC SERIES CONTACTOR (AVERAGE OF EIGHT SEPARATE RUNS)

| Organic Substance | Ozone | | | No Ozone | | |
|---|---|---|---|---|---|---|
| | μg/L In | μg/L Out | % Change | μg/L In | μg/L Out | % Change |
| Vinyl chloride | 5.4 | 0.65 | 88 red. | 3.86 | 4.33 | 12 inc. |
| Trans 1,2-dichloroethene | 0.73 | 0.0 | 100 red. | 0.57 | 0.55 | 3 red. |
| 1,1-dichloroethane | 7.17 | 5.67 | 22 red. | 4.2 | 3.71 | 12 red. |
| cis 1,2-dichloroethene | 23.4 | 6.2 | 73 red. | 18.6 | 21.0 | 13 inc. |
| trichloroethylene | 0.51 | 0.18 | 65 red. | 0.47 | 0.39 | 17 red. |
| chlorobenzene | 1.36 | 0.3 | 78 red. | 1.01 | 0.8 | 20 red. |
| p-chlorotoluene | 0.36 | 0.0 | 100 red. | 0.35 | 0.12 | 79 red. |
| p-dichlorobenzene | 0.27 | 0.0008 | 97 red. | 0.15 | 0.1 | 33 red. |
| o-dichlorobenzene | 0.32 | 0.038 | 88 red. | 0.3 | 0.17 | 43 red. |
| TOC | 8.15 | 7.60 | 7 red. | 7.56 | 7.48 | 2 red. |
| THMFP | 288 | 397 | 38 inc. | 388 | 503 | 30 inc. |

Ozonated air, resulting in an average absorbed ozone dose of 4.25 mg/L, reduced 5.4 μg/L vinyl chloride in the influent to 0.65 μg/L in the effluent, a reduction of 88%. When air alone was used we averaged an increase of 12 percent. Table 20 confirms that all double-bond halogenated compounds are reduced by ozonation, with varying lower values associated with the effect of aeration alone.

As in previous work, 1,1-dichloroethane, a saturated compound, was only reduced 22 percent by ozonation, versus 12 percent by air alone. Double bond compounds were reduced to lower levels (Table 18) when the absorbed ozone dose was 14.5 mg/L. In Tables 18 and 20, there are 8 double-bond halogenated compounds. Only three were present above 1 μg/L concentration in the influent. These were, in descending level, cis 1,2-dichloroethene, vinyl chloride and chlorobenzene. At an absorbed ozone dose of 14.5 mg/L (Table 18) these three compounds were reduced 90, 91 and 94 percent, respectively. At an absorbed ozone dose of 4.25 mg/L (Table 20) they were reduced 73, 88 and 78 percent, respectively. Thus we observe a dosage response.

We also followed the effect on TOC and THMFP. Ozonation reduced the TOC level from 8.15 to 7.6, a 7% reduction. Air alone reduced the TOC level from 7.56 to 7.48 ppm, a 2% reduction. The THMFP data are very interesting. Ozonation increased the THMFP values from 288 μg/L entering to 397 μg/L in the effluent, an increase of 38%. Air alone increased the THMFP values from 388 μg/L entering to 503 μg/L in the effluent, an increase of 30%. Thus air alone increases the level of THMFP in our water 80% of the value achieved by ozonation.

This set of eight experimental runs thus confirms our general finding in the 172-day-test run in the pilot plant (e.g., air alone increases the THMFP of our water. The total holding time in the MOC-BOC series is approximately 11 minutes. Of course, any dissolved oxygen could react further in the sample bottles after the samples are taken.

It should be noted that in PS 1, an increase in THMFP was not observed as in PS 2 between lime-softened water and the clearwell effluent water. Differences between the two studies are shown in Table 21. In PS 1, the lime-softened water and clearwell recarbonated water THMFP levels were 427 and 438 μg/L, respectively. An increase of 7 percent THMFP occurred in the ozone contactors. In comparison, in PS 2 the values were 290 and 518 μg/L with a 13-percent increase. There may be a possible explanation for the increase in one case and not the other. PS 1 was run from September 9, 1980, to February 27, 1981. This period in South Florida is within the dry season. Recharge to wells during this period has a higher percentage of surface water from canals. This surface water would have been exposed to air, which could result in conversion of the most readily converted TOC substances to THMFP substances. When such recharge water was pumped from the wells, one might expect that further oxygen picked up in the plant process between the lime-softener and the clearwell effluent would have less effect on further THMFP buildup. Notice that in Table 16, the raw water TOC and THMFP levels were higher in PS 1.

## TABLE 21

## MAJOR DIFFERENCES BETWEEN PS 1 AND PS 2 THAT WOULD EFFECT COMPARATIVE CONCLUSIONS

| Pilot Study | Test Length In Days | Test Period Run Dates | Average Absorbed Ozone Dose mg/L |
|---|---|---|---|
| 1 | 160 | 09/09/80 to 02/27/81 | 11.3 |
| 2 | 172 | 05/05/81 to 11/06/81 | 14.5 |

### TOC PROFILE (ppm)

| Pilot Study | Raw Water | Lime-Softened Water | Clearwell Recarbonated Water | Ozone Contactor Effluent Water |
|---|---|---|---|---|
| 1 | 10.6 | 7.8 | 7.7 | 6.7 (13% reduction) |
| 2 | 9.3 | 7.0 | 6.77 | 6.15 (09% reduction) |

### THMFP PROFILE (μg/L)

| Pilot Study | Raw Water | Lime-Softened Water | Clearwell Recarbonated Water | Ozone Contactor Effluent Water |
|---|---|---|---|---|
| 1 | 586 | 427 | 438 | 467 (07% increase) |
| 2 | 392 | 290 | 518 | 585 (13% increase) |

PS 2 was conducted during the wet season of the year. Recharge during this period results from a higher percentage of rain water, which percolates through the porous soil (anaerobic conditions), leaching TOC substances. It is conceivable that such water when pumped into the water treatment plant would contain TOC substances which might be more readily converted to THMFP substances by adsorbed oxygen. Only further studies will determine if such is the case.

TOC--

The level of TOC entering the ozone contactors is plotted in Figure 31 (labeled influent TOC from clearwell + recarbonation). The level of TOC in the (MOC-BOC effluent is also plotted in Figure 31. For the first 7.6 test days, the average TOC level in and out was 10.7 and 9.42 ppm, respectively, a reduction of 12 percent by ozonation. For the remainer of the testing period, the average TOC level in and out was 6.77 and 6.15 ppm, a reduction of 9 percent by ozonation. This 9 percent reduction agrees closely with the 7 percent reduction shown in Table 20.

THMFP--

The level of THMFP entering and leaving the ozone contactors is plotted in Figure 30. Over the entire 172 day test period, the average increase in THMFP occurring in the ozone contactors was 13 percent. This compares with an increase of 18 percent (38 percent increase for ozone minus 30 percent increase for air alone) in the 8 sample runs discussed in Table 20.

## Pilot Plant Section III Chemical Data

Dissolved Oxygen--

From PS 1, we knew the proper level of oxygen (adjusted by flow meter) to add to the sampling points in each BAC tower to achieve a DO level of at least 6 ppm in the BAC tower effluent. However, with virgin GAC in both BAC towers at the start of the test period in PS 2, this oxygen level could not maintain the desired DO level in the effluent for the first few days after initial startup. The level of DO in the three level sampling points in each BAC tower, 2.5, 5 and 10 ft., is shown in Table 14.

Two to three days were required for the DO level to reach the desired concentration. After this time, in both BAC towers, the DO levels at the 2.5-and 5-ft. sampling points averaged 12 and 6 ppm at the 10-ft. sampling point.

Turbidity--

In the nonozone-BAC tower (Table 15), the turbidity was only slightly decreased over the value entering. In the ozonated tower, the turbidity value was only slightly increased.

Color—

There was a slight decrease in color (Table 16) in the effluent water from both BAC towers.

pH—

There was a slight decrease in pH in the nonozone-BAC tower effluent (Table 17) and almost a whole pH unit decrease in the ozone-BAC tower effluent.

Halogenated Organics—

The time in days for Breakthrough (B.T.) and Saturation (Sat.) for halogenated organics in this study is shown in Table 22. No conclusions have been drawn.

TOC—

TOC data for Section III of the pilot plant are plotted in Figures 31 through 37. Many experimental factors must be considered in evaluating these data: (1) the variability of the entering TOC level on a daily basis, as well as an average of 9 percent less TOC entering the ozone-BAC tower (reduced in the ozone contactors), (2) breakthrough and plateau saturation times of the TOC substances as a whole on the carbon, (3) initial startup conditions, and others. Since the ozone-BAC tower received an average of 9 percent less TOC than the nonozone-BAC tower, it would be difficult to compare the performance of the two BAC towers alone. Initial comparison is based only on the effluent levels of TOC from each system, the nonozone-BAC versus the ozone-BAC system. It would also be difficult to compare the performance of the BAC tower in PS 1 and PS 2 since the influent TOC levels were different.

In Figure 31, the TOC profile is presented for the 2.5, 5 and 10 ft. bed depths in the nonozone-BAC tower. The three curves are compared with the influent TOC level to the column. As in previous work, even from initial startup, we observe breakthrough of some of the TOC at all bed depths. We then observe the typical S-shape adsorption isotherm curve for each bed depth, reaching what has been called a "plateau" level, below the influent level. However, as in previous work, it is again apparent that this is not a true "plateau" (flat saturation), but the beginning of a portion of the breakthrough curve showing a slower approach to the influent TOC level. We believe that in time, the effluent TOC level will indeed reach the influent level (this was shown in PS 1). We observe that in Figure 31, we are nearing this condition at 172 days at the 2.5 ft. bed depth. At 5 and 10 ft., as expected, we are not as close to the influent level at 172 days. In Figure 31, at initial start-up, approximately 0.5 ppm of TOC passes directly through all bed depths of carbon. For each bed depth the initial plateau level (lower for increasing bed depths) was reached at approximately 5, 10, and 25 days for 2.5, 5 and 10 ft. of bed depth respectively. Similar results are observed in Figure 32 for the ozone-BAC tower. At the end of the test period, the three curves in Figure 32 are not as close to the influent level curve as was

## TABLE 22

## HALOGENATED ORGANIC COMPOUND BREAKTHROUGH AND COLUMN SATURATION DATA (PS 2)

| Sample Point | Vinyl Chloride | | Trans 1,2-Dichloroethene | | 1,1-Dichloroethane | | Cis, 1,2-Dichloroethene | | Trichlorothylene | | Chlorobenzene | | P-chlorotoluene | | P- and O-dichlorobenzene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | B.T.* | SAT.* | B.T. | SAT. | B.T. | SAT. | B.T. | SAT. | B.T. | SAT. | B.T. | SAT. | B.T. | SAT. | B.T. | SAT. |
| Nonozone-BAC tower "D" | | | | | | | | | | | | | | | | |
| 2.5 ft. | 7.6 | 17.4 | 34.3 | 118 | 37.3 | 80 | 28.5 | | 44 | 69 | 44 | N.R. | N.R. | N.R. | 98 | N.R. |
| 5 ft. | 10.5 | 28.5 | 51 | N.R. | 51 | 91 | 23.5 | 51 | 95 | N.R. | 91 | N.R. | N.R. | N.R. | N.R. | N.R. |
| 10 ft. | 23.5 | 23.5 | 91 | N.R. | 37 | 107 | 34.3 | 68 | 48 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| Ozone-BAC tower "C" | | | | | | | | | | | | | | | | |
| 2.5 ft. | 7.6 | 17.4 | 30.3 | 78 | 7.6 | 80 | 7.6 | 37.3 | 30.3 | 69 | 169 | N.R. | N.R. | N.R. | N.R. | N.R. |
| 5 ft. | 21.5 | 30.3 | 48 | 78 | 3.6 | 95 | 44 | N.R. | 48 | N.R. | 148 | N.R. | N.R. | N.R. | N.R. | N.R. |
| 10 ft. | 7.6 | 48 | 34 | 48 | 51 | 98 | 44 | N.R. | 48 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |

B.T. = Breakthrough
SAT. = Saturation
N.R. = Not reached

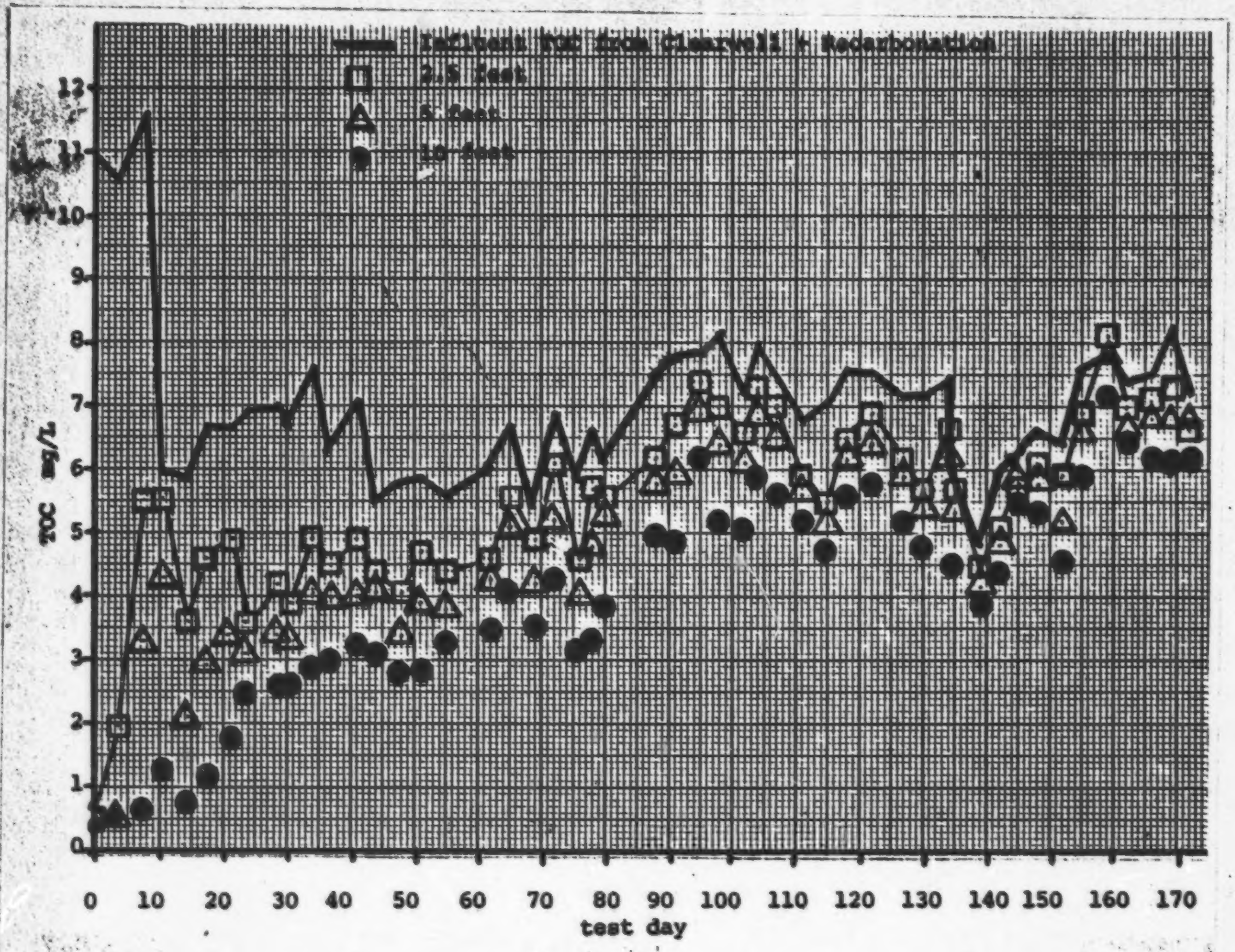


Figure 31. TOC effluent from 2.5, 5 and 10 ft. of bed depth from nonozone-BAC tower.

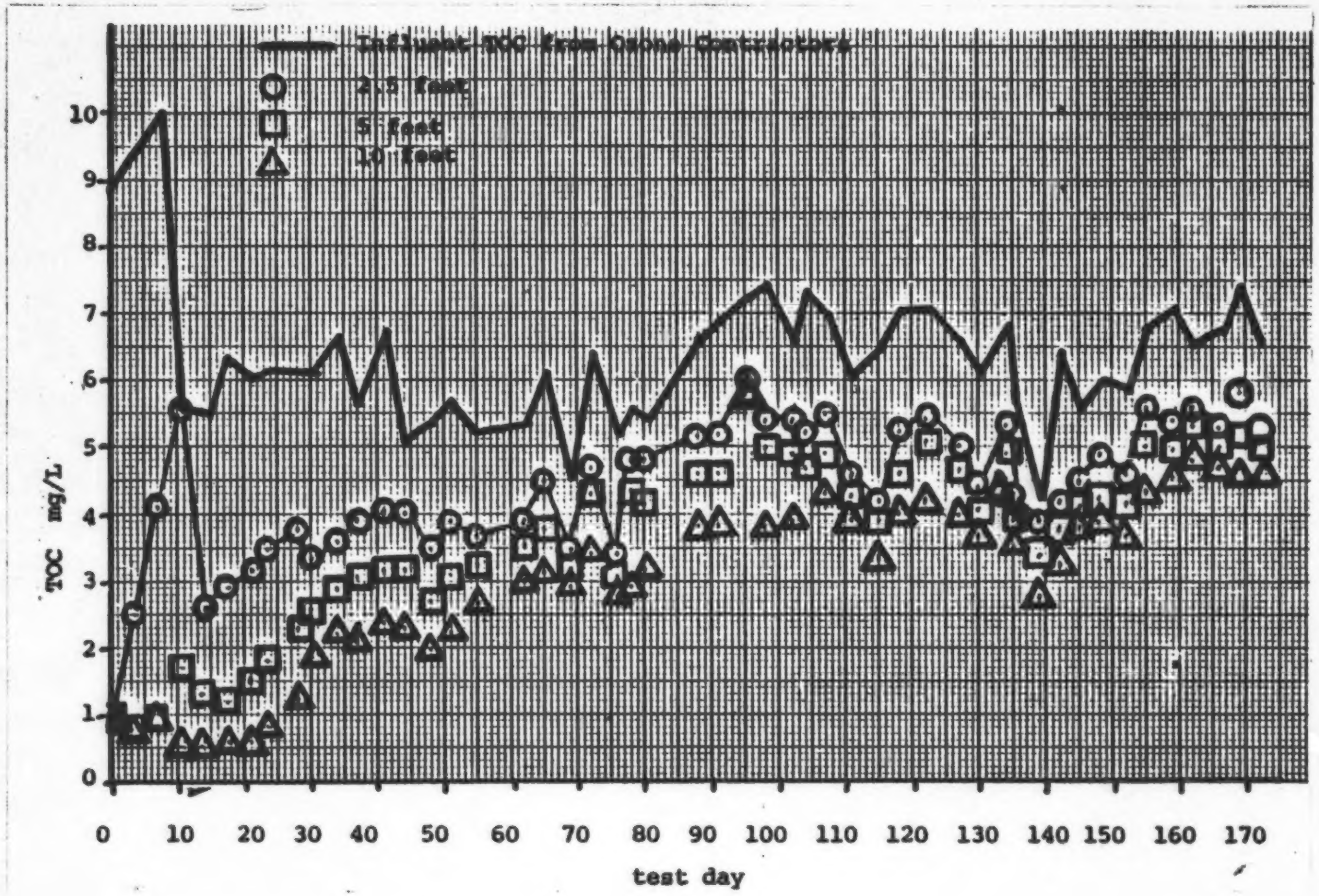


Figure 32. TOC effluent from 2.5, 5 and 10 ft. of bed depth from ozone-BAC tower.

$$\frac{\text{TOC effluent 2.5 ft. of nonozonated BAC Tower}}{\text{TOC influent}} \times 100 = \begin{array}{l}\text{Percent difference of}\\ \text{TOC nonozonated BAC Tower}\\ \text{effluent compared to influent}\end{array}$$

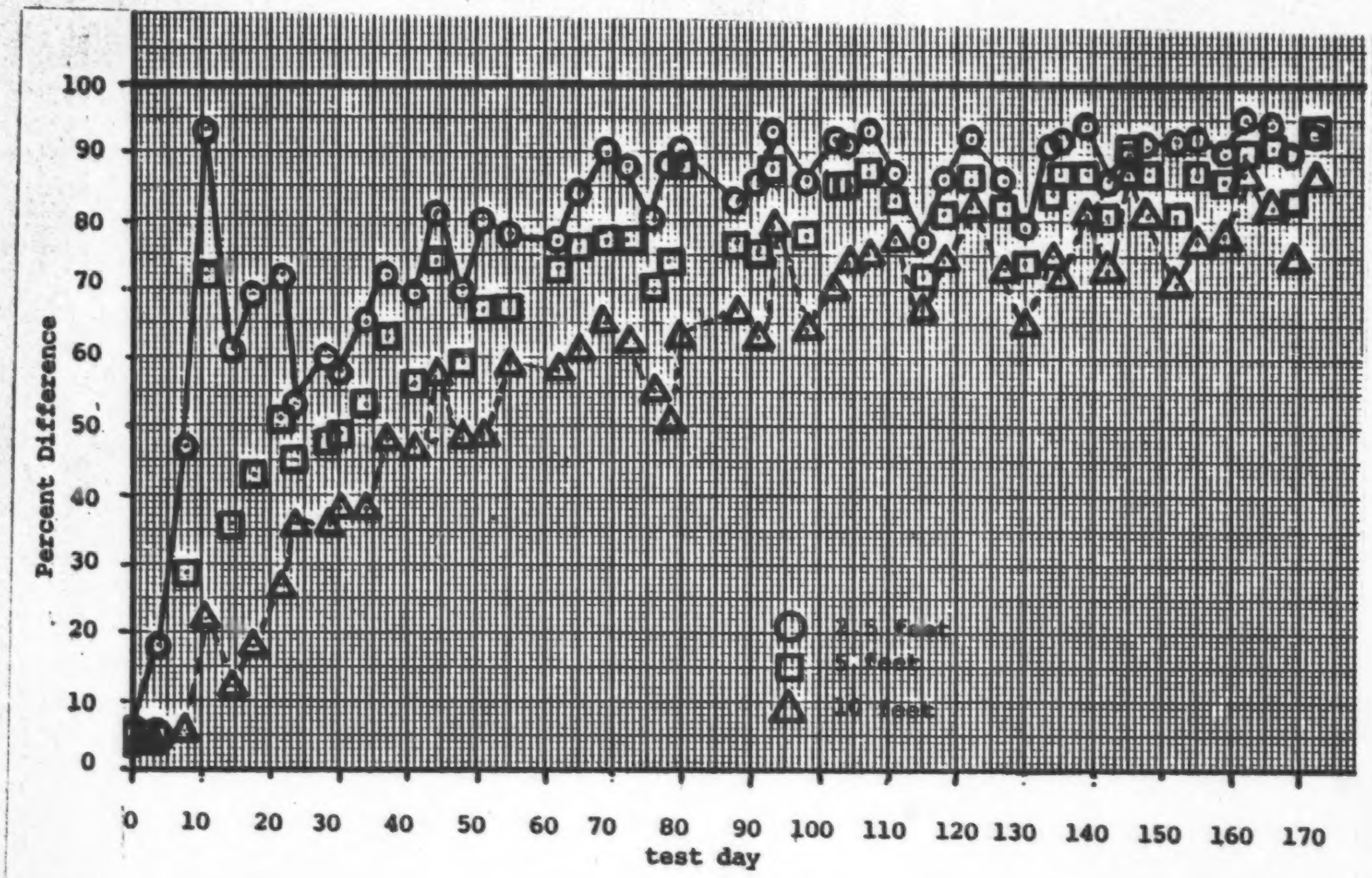


Figure 33. TOC effluent from 2.5, 5 and 10 ft. of bed depth from nonozone-BAC tower compared with TOC influent.

$$\frac{\text{TOC effluent 2.5 ft. ozonated BAC Tower}}{\text{TOC influent}} \times 100 = \text{Percent difference of ozonated BAC Tower compared to influent}$$

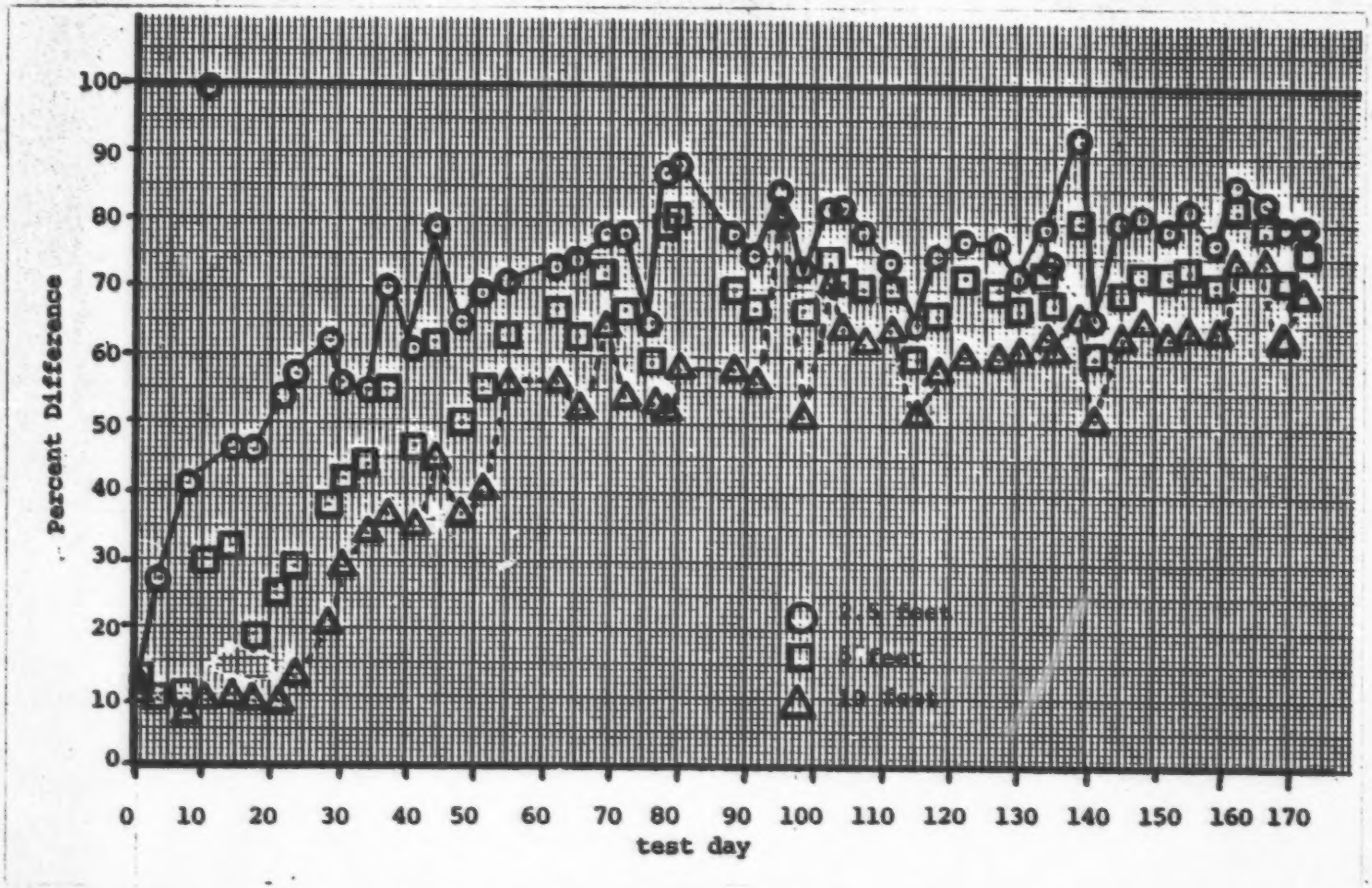


Figure 34. TOC effluent from 2.5, 5 and 10 ft. of bed depth from ozone-BAC tower compared with influent.

$$\frac{\text{TOC effluent 2.5 ft. of ozonated BAC Tower}}{\text{TOC effluent 2.5 ft, of nonozonated BAC Tower}} \times 100 = \begin{array}{l}\text{Percent difference of}\\ \text{ozonated BAC Tower}\\ \text{compared to nonozonated}\\ \text{BAC Tower}\end{array}$$

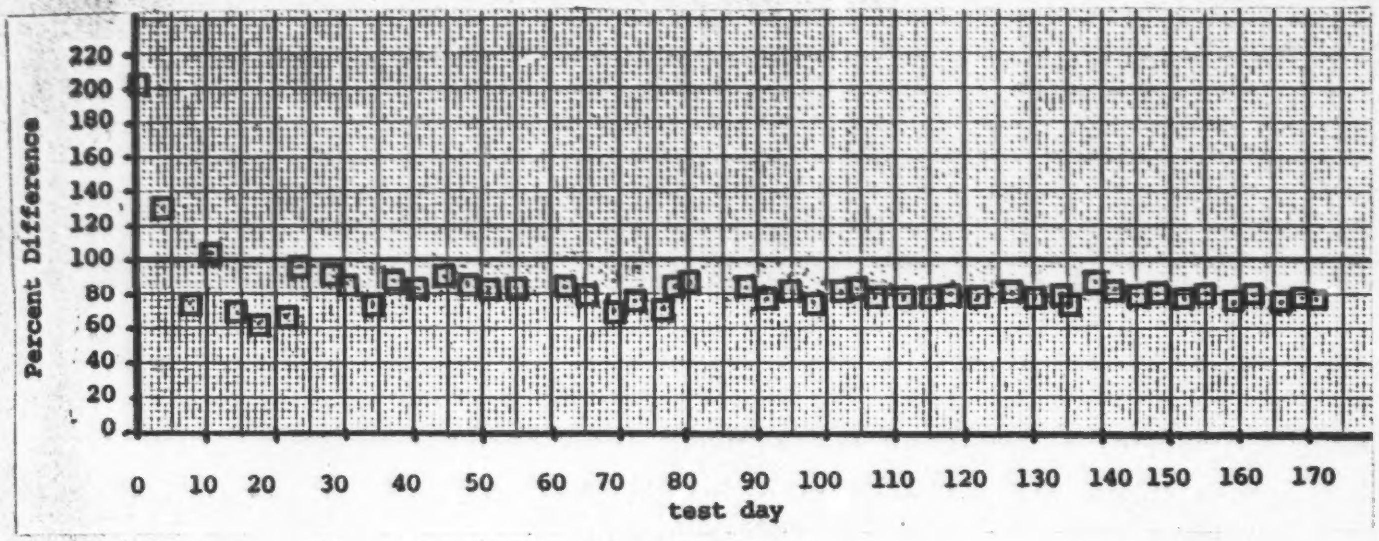


Figure 35. TOC effluent from 2.5 ft. of bed depth of ozone-BAC tower compared with TOC effluent from 2.5 ft. of bed depth of nonozone-BAC tower.

$$\frac{\text{TOC effluent 5-ft. depth ozonated BAC Tower}}{\text{TOC effluent 5-ft. depth nonozonated BAC Tower}} \times 100 = \text{Percent Difference of ozonated to nonozonated effluent}$$

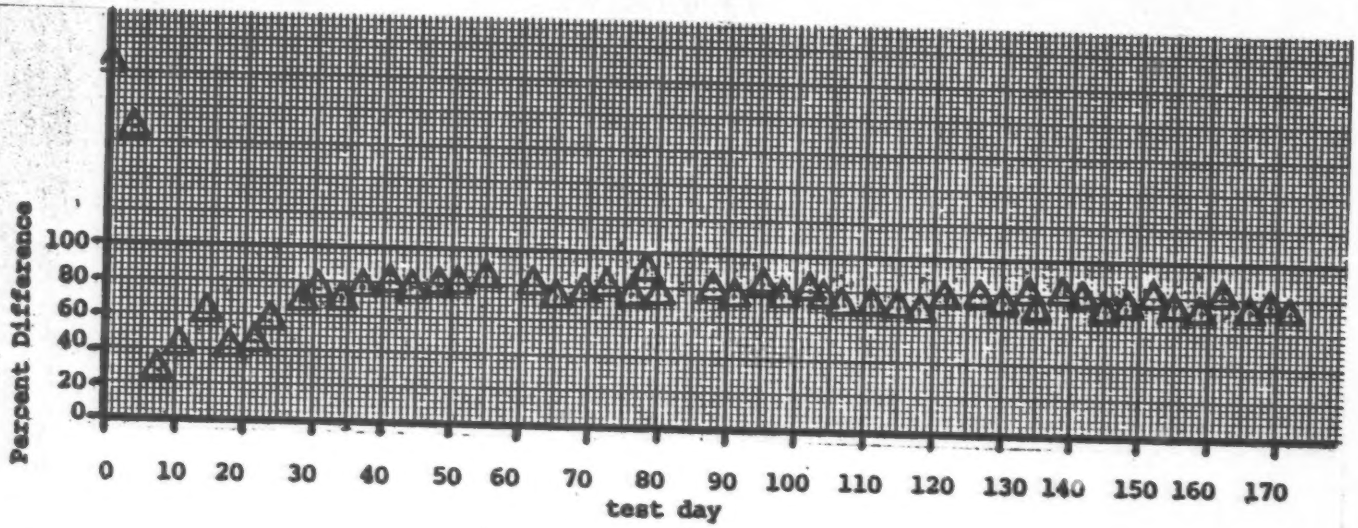


Figure 36. Percent difference in TOC levels of ozonated and nonozonated effluents from 5 ft. of BAC tower.

$$\frac{\text{TOC effluent 10-ft. depth ozonated BAC Tower}}{\text{TOC effluent 10-ft. depth nonozonated BAC Tower}} \times 100 = \text{Percent difference of ozonated to nonozonated effluent}$$

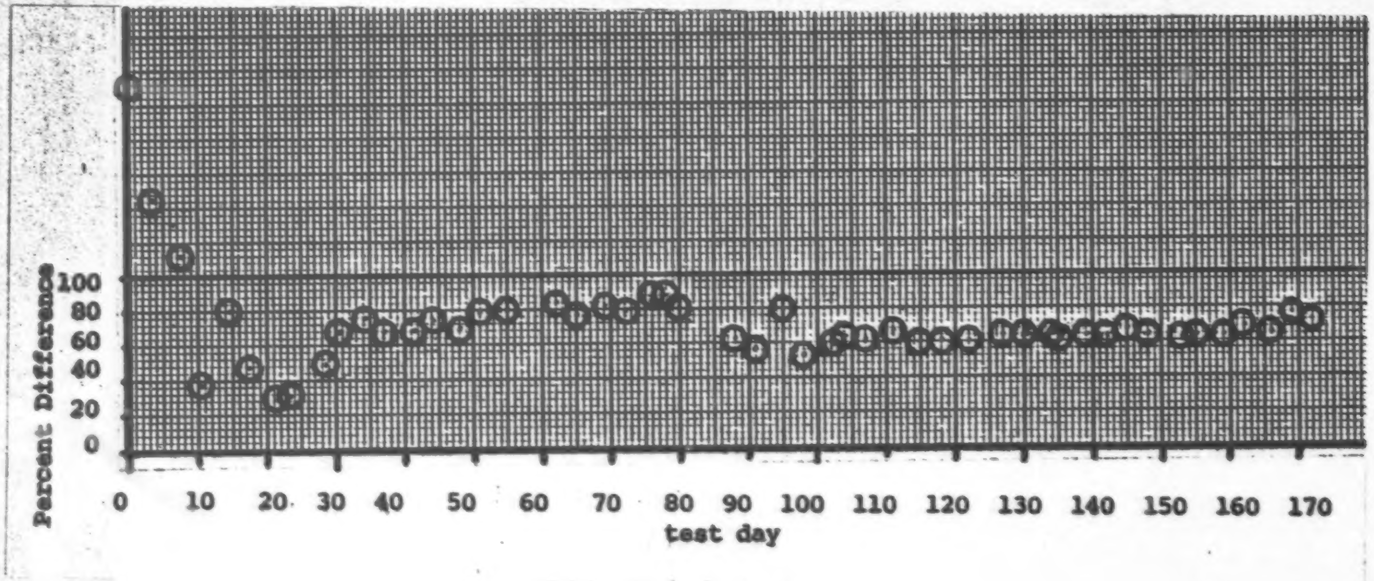


Figure 37. Percent difference in TOC levels of ozonated and nonozonated effluent from 10 ft. of BAC tower.

the case in Figure 31 for the nonozone-BAC tower. To compare the performances of effluent TOC level for both systems, we can also look at the data in another way. We can take the effluent TOC level for a single bed depth in the ozonated tower divided by the effluent TOC level for the same bed depth on the nonozonated tower, times 100 to get the percent differences between the two towers. These data are plotted in Figures 38 and 39 for 2.5, 5 and 10 ft. bed depth. We observe again the effect of the S-shaped adsorption curve with the top of the elongated "S" gradually nearing the influent TOC level, but approaching more slowly in the ozone-BAC system. Again, we cannot say how much of the improvement is due to the 9 percent lower level of TOC entering, the modification of the TOC substances by ozone on adsorption, or the provision of a better food for the bacteria. It is even difficult with the plots in Figures 33 and 34 to give a quantitative relationship to the experiment. Perhaps this can be better accomplished by still looking at the data in another way. In Figures 35 through 37 for each bed depth we are plotting the ozone-BAC TOC level, divided by the nonozone-BAC TOC level, times 100. In these plots we should not be concerned with the first two or three test day results. In this period, both systems passed low levels of TOC. A look at the raw data will show that with such low TOC values passed, it is not significant that the percent difference is higher for the ozone-BAC system. This will also apply to the THMFP data to be presented next. We observe in these plots, Figures 35 through 37, that from approximately test day 30 on, we see a rather flat response curve. Averaging the response, we obtain the values in Table 23.

TABLE 23

COMPARISON OF TOC REMOVAL BY THE OZONE-BAC AND NONOZONE-BAC SYSTEMS (PS 2)

PERCENT DIFFERENCE FOR EACH BED DEPTH = $\frac{\text{TOC IN EFFLUENT FROM OZONATED-BAC SYSTEM}}{\text{TOC IN EFFLUENT FROM NONOZONATED BAC SYSTEM}} \times 100$

| Bed Depth | From Test Day 30 TO 172 | From Test Day 30 TO 80 | From Test Day 80 TO 172 |
|---|---|---|---|
| 2.5 Ft. | 80 | | |
| 5 Ft. | 78 | | |
| 10 Ft. | 69 | 78 | 64 |

From test day 30 to 172, with increasing bed depth we observe that for 2.5 ft., 5 ft. and 10 ft., respectively, the ozone-BAC system TOC effluent level was 80 percent, 78 percent and 69 percent of the value for the nonozone-BAC system. In Figure 37, the plateau portion may have two zones, from day 30 to day 80, and from day 80 to day 172. The average levels for these two zones are shown in Table 23.

The accumulated TOC data are plotted in Figures 40 through 43. Accumulated TOC influent to the nonozone-BAC tower and accumulated TOC in the effluent for each bed depth are shown in Figure 38. Similar plots are shown in Figure 39 for the influent to the ozone-BAC tower and the effluent from each bed depth. The accumulated TOC influent to the nonozone-BAC tower and the accumulated TOC removal by each bed depth are shown in Figure 44. The accumulated TOC influent to the ozone-BAC tower and the accumulated TOC removal by each bed depth are shown in Figure 45. For comparison, the curves from Figure 42 are shown in Figure 43 (dashed lines). As in PS 1, the nonozone-BAC curves appear to level off faster than the ozone-BAC curves. Also as in PS 1, the ozone-BAC tower removed more TOC than the nonozone-BAC tower, even though it received less TOC.

A comparison of accumulated TOC data for both BAC towers is shown in Figure 46. The accumulated TOC removal for each bed depth (X-axis) is plotted versus the accumulated TOC influent (Y-axis). As in PS 1, for a given influent, the ozone-BAC tower removed more TOC than the nonozone-BAC tower.

THMFP —

THMFP data for Section III are plotted in Figures 40 through 43 and 47 through 49. As with interpretation of TOC data, many experimental factors must be considered, again the daily variability of the influent THMFP levels and the 13 percent average increases in THMFP loading on the ozone-BAC tower (compared with the influent on the nonozone-BAC tower - a result of passage through the MOC-BOC system). Once again, initial comparison is made only on the overall effluent THMFP levels of both complete systems.

The effluent THMFP levels from 2.5, 5 and 10 ft. bed depths from the nonozone-BAC tower are plotted in Figure 40, with the influent THMFP level curve (average THMFP influent was 518 µg/L). Similar THMFP data for the ozone-BAC tower are plotted in Figure 41, with the influent THMFP level (average THMFP influent was 516 µg/L, 13 percent above the average influent to the nonozone-BAC towers). In both Figures 40 and 41, note the expected pattern of THMFP adsorption on the carbon, initially a high percentage of removal followed by decreasing removal in an S-shaped curve to a beginning plateau region, followed by a gradual rise toward saturation.

In Figure 42, the THMFP effluent levels at 2.5, 5 and 10 ft. bed depths, divided by the influent THMFP level times 100 are plotted for the nonozone-BAC system. The ozone-BAC system is plotted in Figure 43. Again, in both figures we observe the expected S-shaped adsorption curves. Again, the ozone-BAC system (Figure 43), while receiving 13 percent more THMFP, shows more adsorptive capacity (longer time to reach the beginning of the plateau). As with the TOC evaluation, we can plot the THMFP effluent for each bed depth in the ozone-BAC system divided by the effluent in the nonozone-BAC system times 100. These plots are presented in Figures 47 through 49. In all three figures, we observe roughly three zones: A zone of performance from initial startup to day 65, a zone from day 65 to day 122, and a zone from

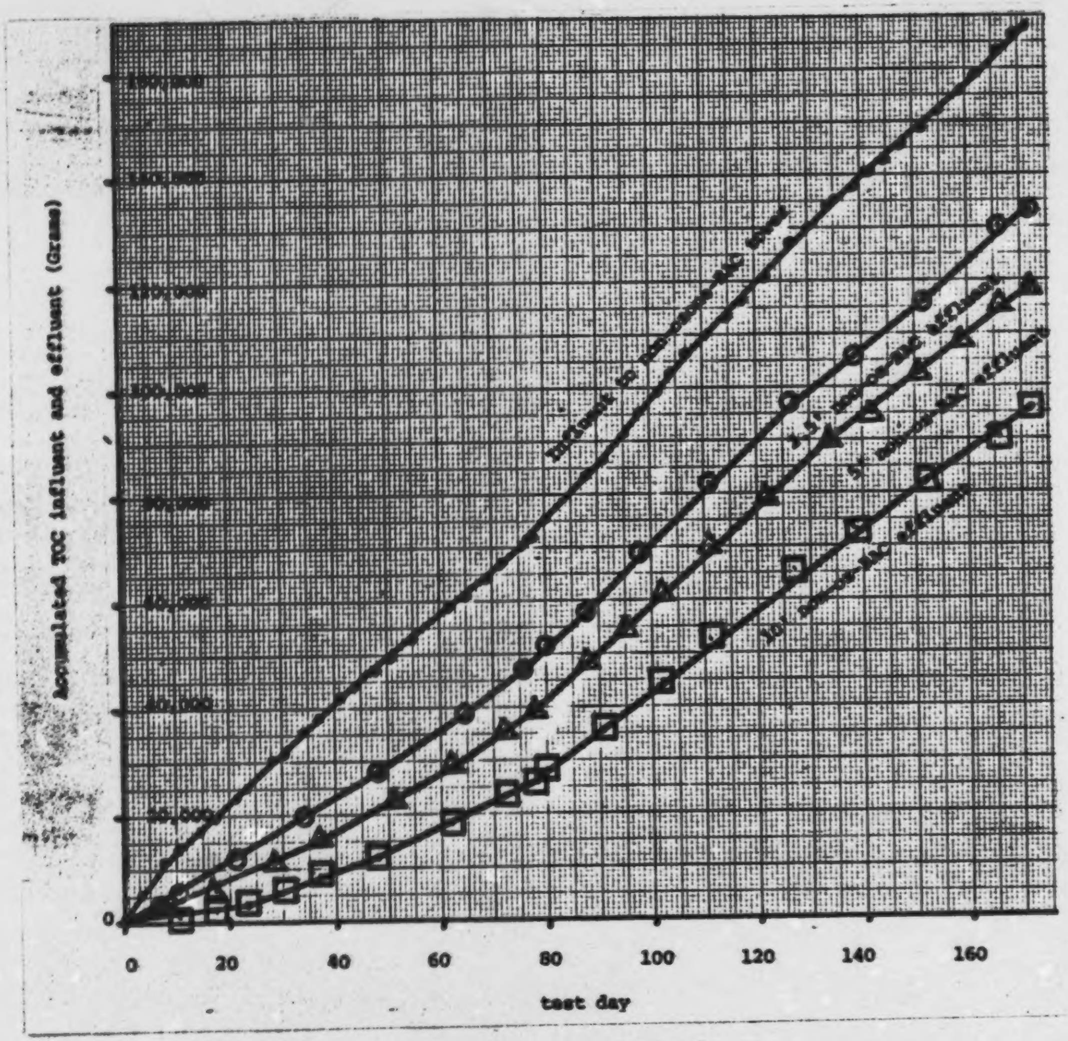


Figure 38. Accumulated TOC influent and effluent (nonozone-BAC tower, PS 2.)

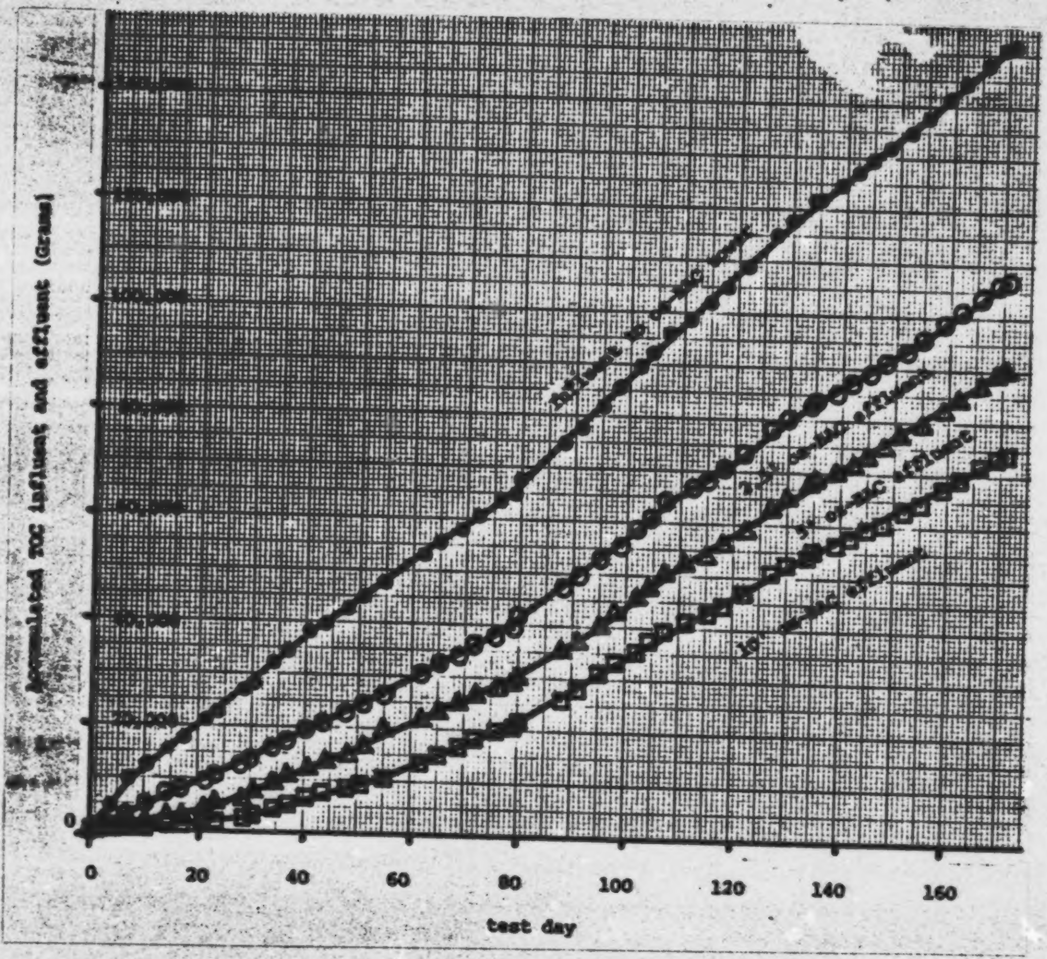


Figure 39. Accumulated TOC influent and effluent (ozone-BAC tower, PS 2).

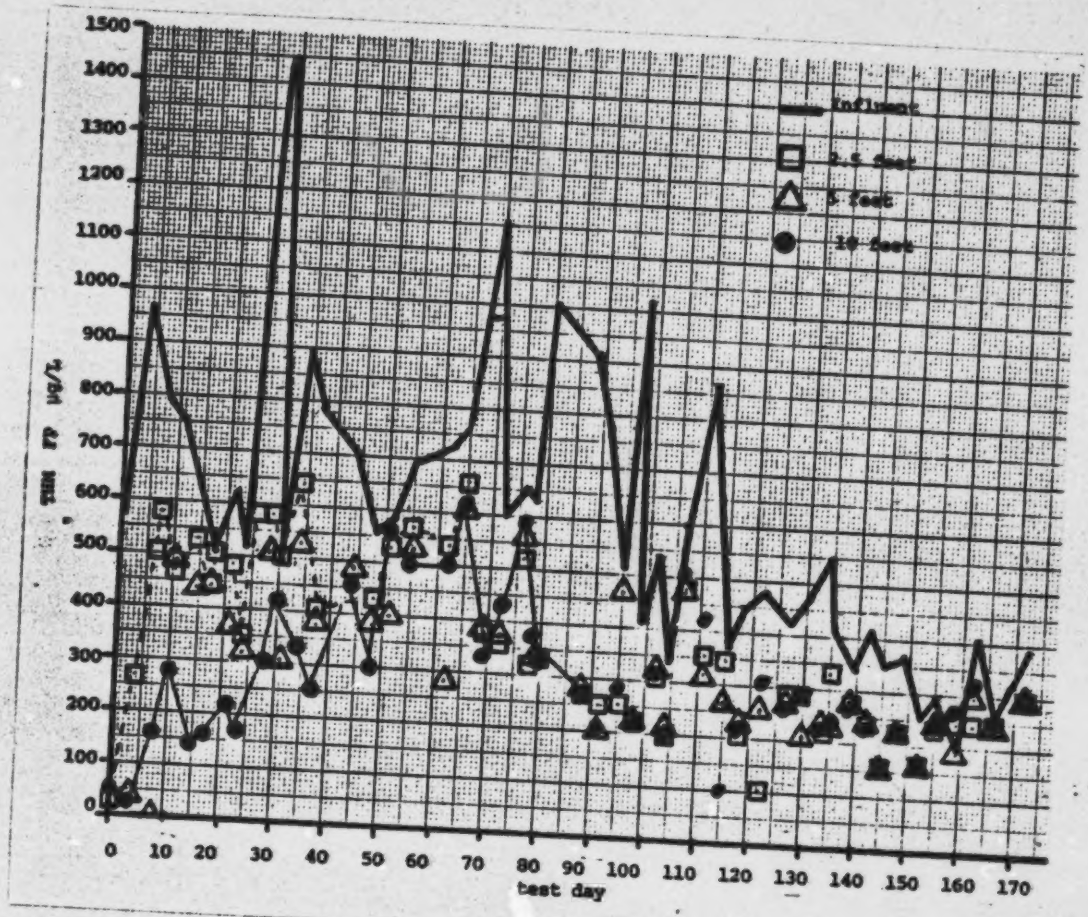


Figure 40. THMFP in nonozone-BAC tower effluent at 2.5, 5 and 10 ft. bed depth.

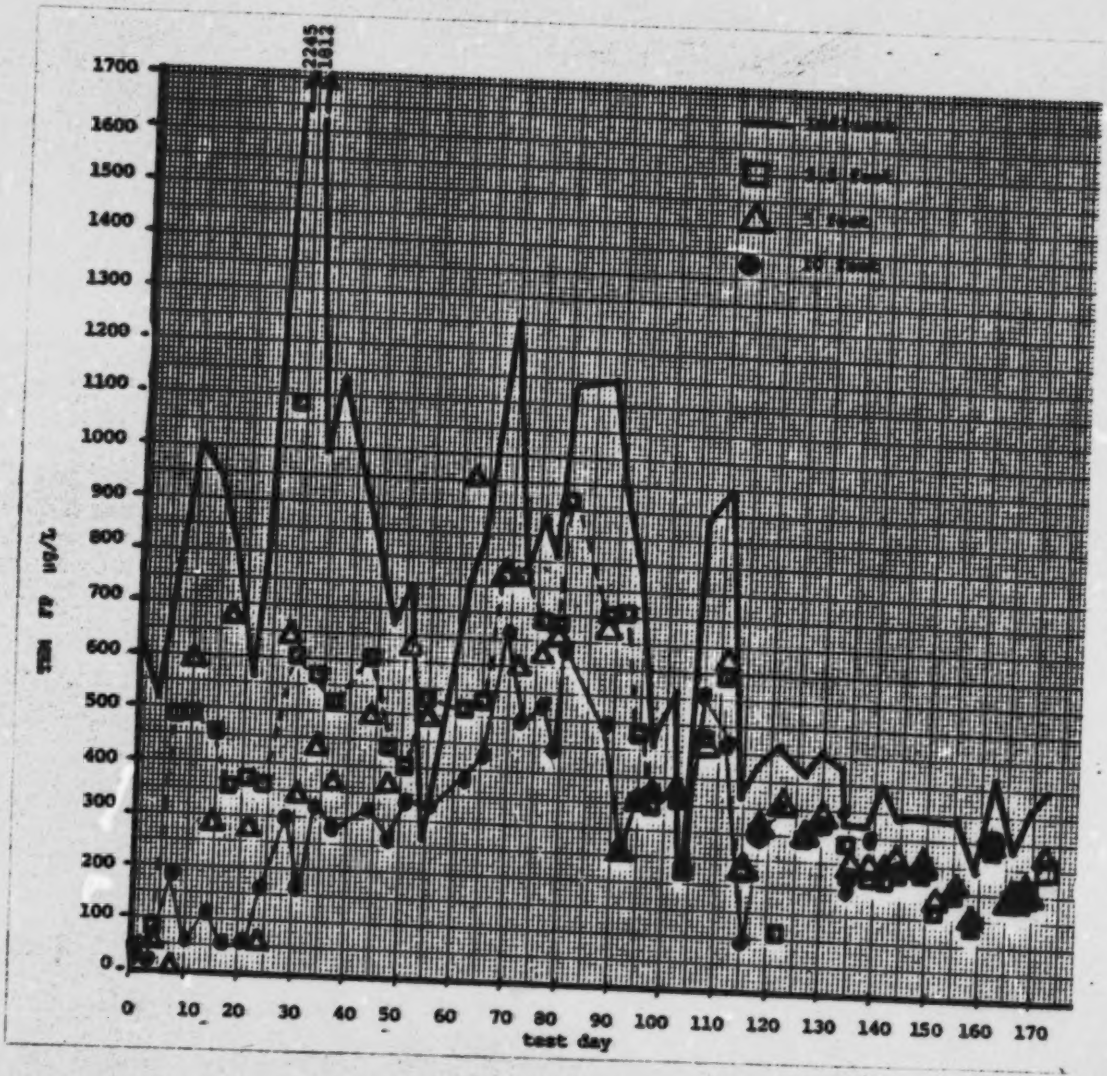


Figure 41. THMFP in ozone-BAC tower effluent at 2.5, 5 and 10 ft. bed depth.

$$\frac{\text{THMFP effluent 2.5 ft. of nonozonated BAC Tower}}{\text{THMFP influent}} \times 100 = \begin{array}{l}\text{Percent difference of}\\ \text{nonozonated BAC Tower}\\ \text{to influent}\end{array}$$

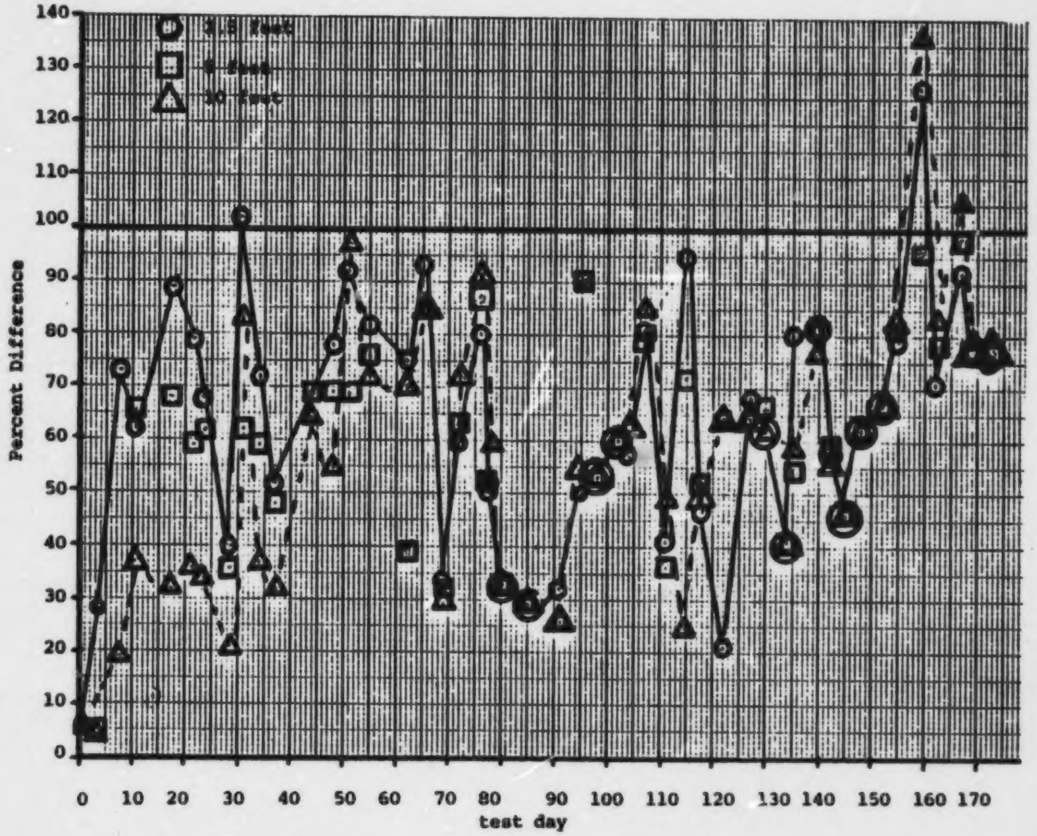


Figure 42. THMFP effluent from 2.5, 5 and 10 ft. bed depth from nonozone-BAC tower compared with influent level.

$$\frac{\text{THMFP effluent 2.5 ft. ozonated BAC Tower}}{\text{Influent}} \times 100 = \text{Percent Difference of ozonated BAC Tower to influent}$$

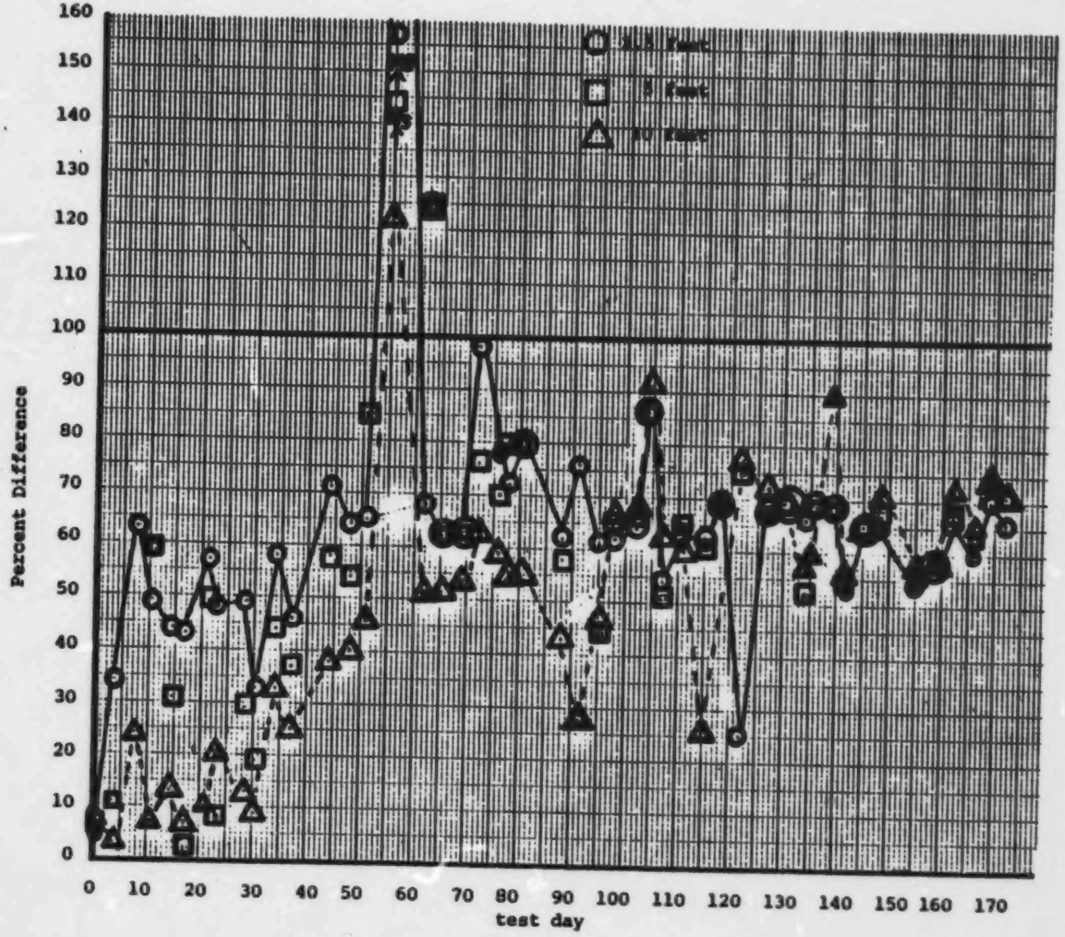


Figure 43. THMFP effluent from 2.5, 5 and 10 ft. bed depth from ozone-BAC tower compared with influent level.

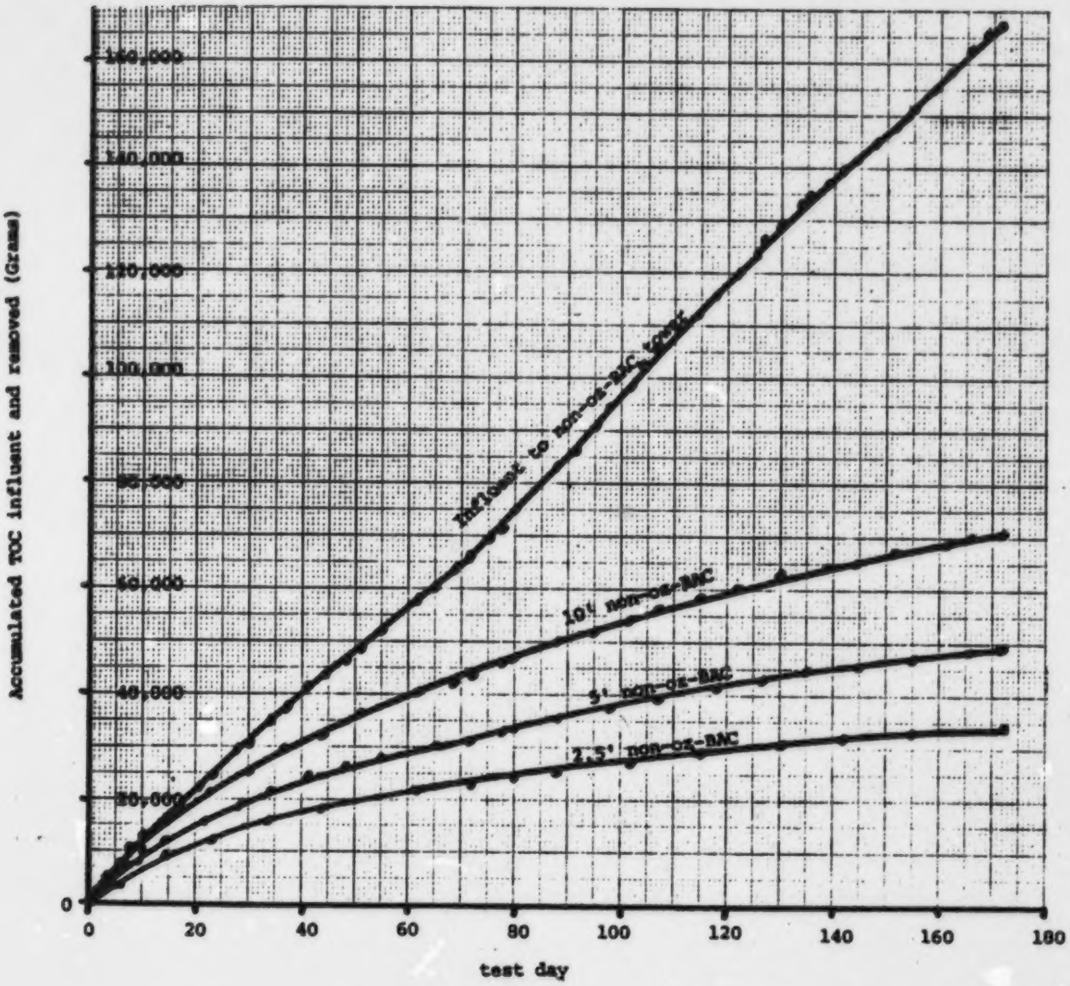


Figure 44. Accumulated TOC influent and removal by nonozone-BAC tower (PS 2).

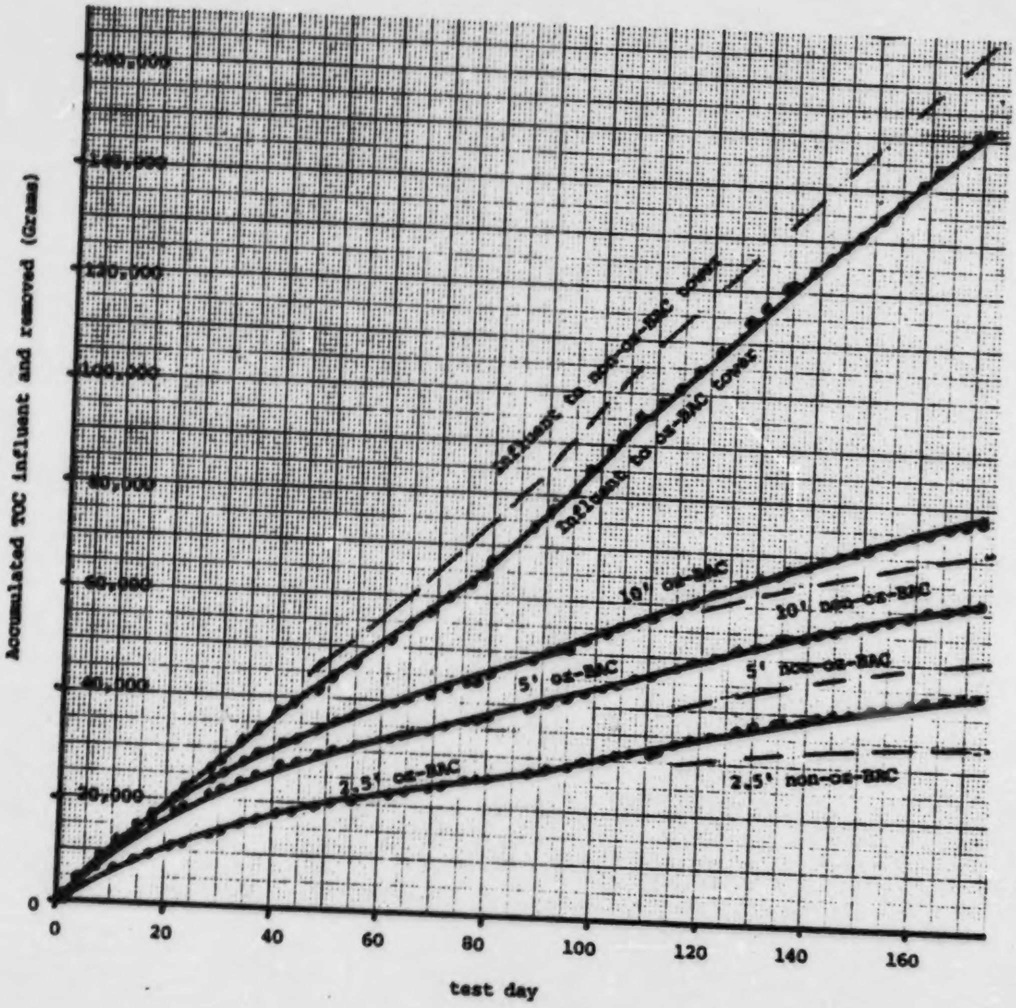


Figure 45. Accumulated TOC influent and removal by ozone-BAC tower (PS 2).

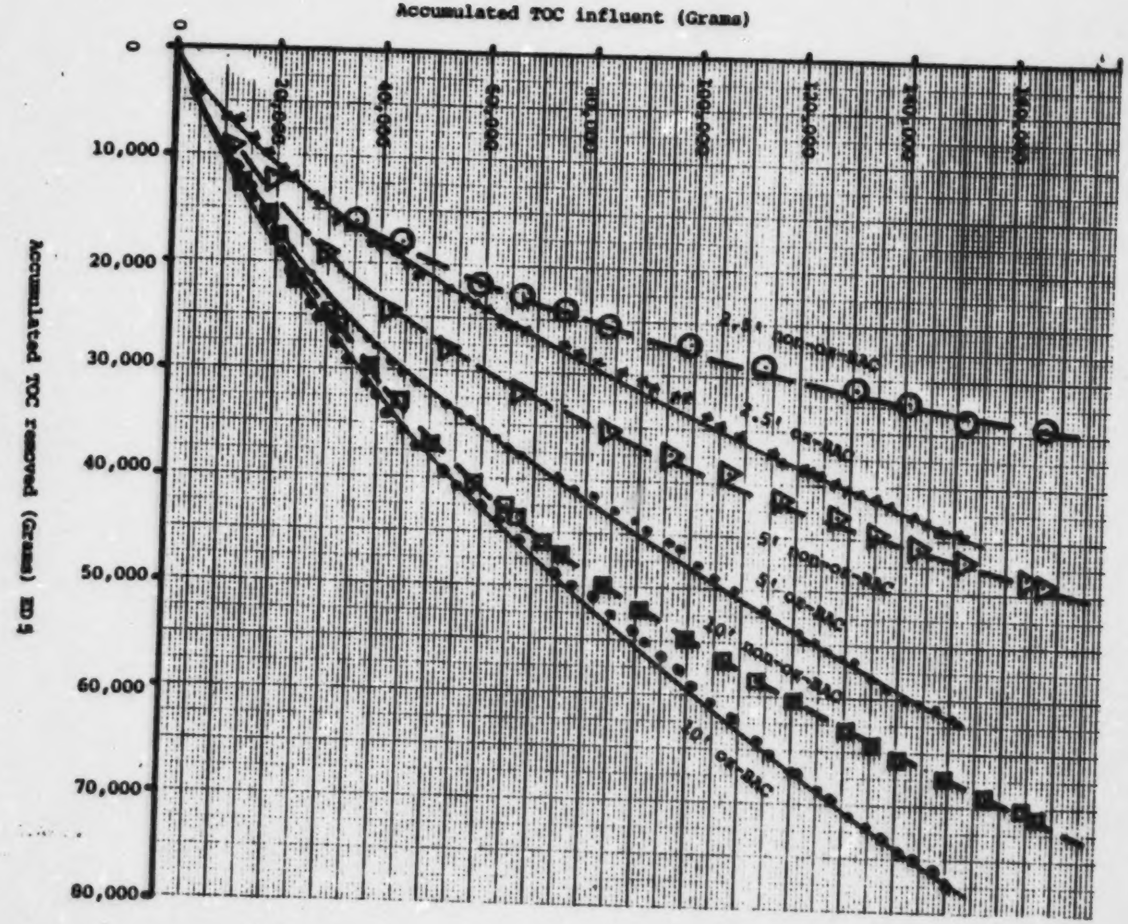


Figure 46. Plot of accumulated TOC influent versus corresponding accumulated TOC removed by BAC towers (PS 2).

$$\frac{\text{THMFP effluent 2.5 ft. of ozonated BAC Tower}}{\text{THMFP effluent 2.5 ft. of nonozonated BAC Tower}} \times 100 = \begin{array}{l}\text{Percent difference of}\\ \text{ozonated BAC Tower effluent}\\ \text{compared to nonozonated}\\ \text{BAC Tower effluent}\end{array}$$

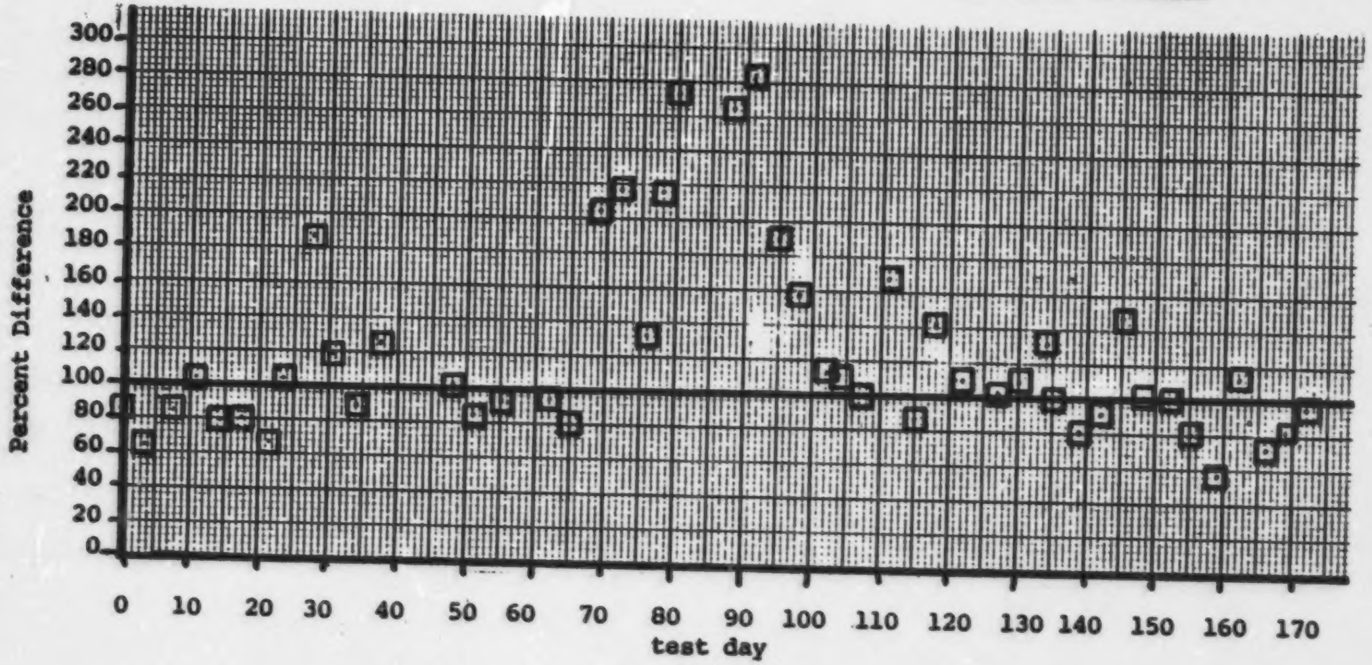


Figure 47. THMFP effluent from 2.5 ft. bed depth of ozone-BAC tower compared with THMFP effluent from 2.5 ft. bed depth of nonozone-BAC tower effluent.

$$\frac{\text{THMFP effluent 5 ft. of ozonated BAC Tower}}{\text{THMFP effluent 5 ft. of nonozonated BAC Tower}} \times 100 = \begin{array}{l}\text{Percent difference of}\\ \text{ozonated BAC Tower}\\ \text{compared to nonozonated}\\ \text{BAC Tower}\end{array}$$

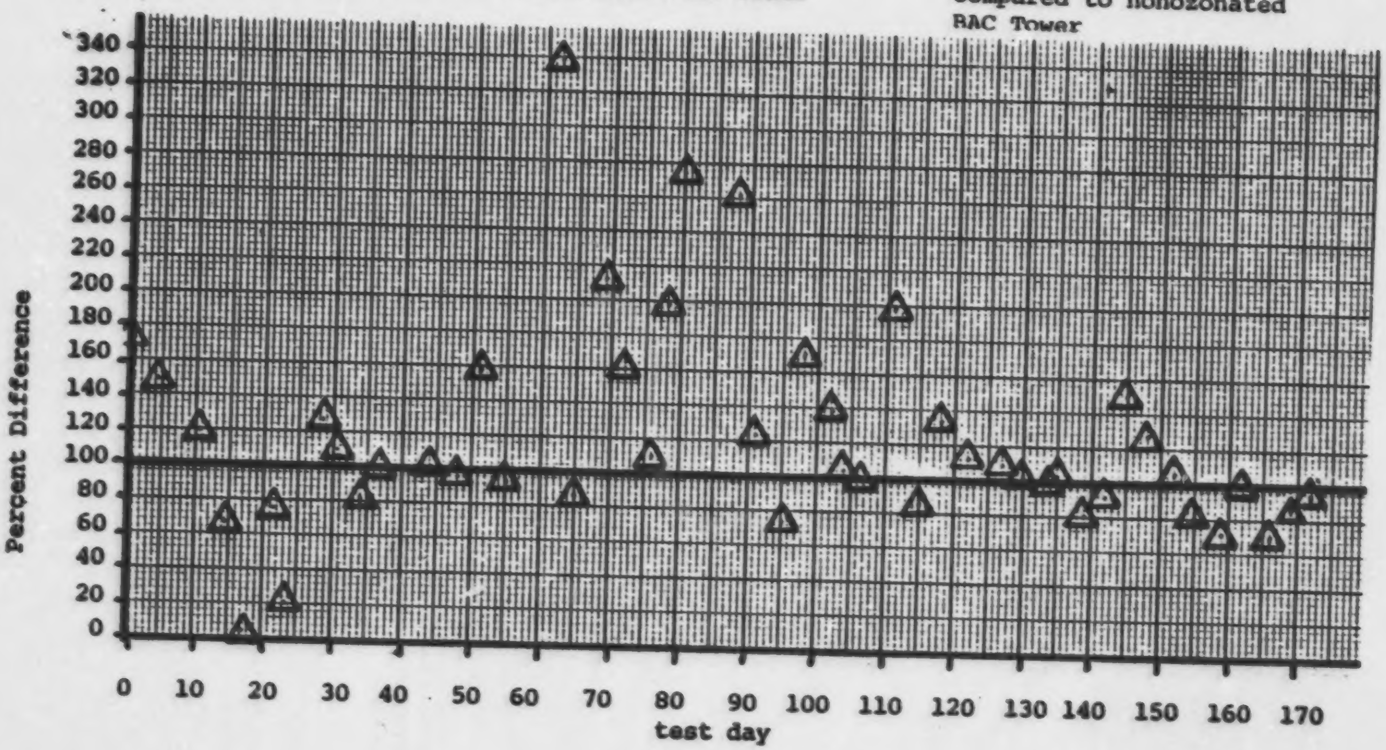


Figure 48. THMFP effluent from 5 ft. of ozone-BAC tower compared with THMFP effluent from 5 ft. of nonozone-BAC tower.

$$\frac{\text{THMFP effluent 10 ft. of ozonated BAC Tower}}{\text{THMFP effluent 10 ft. of nonozonated BAC Tower}} \times 100 = \begin{array}{l}\text{Percent difference of}\\ \text{ozonated BAC Tower}\\ \text{compared to nonozonated}\\ \text{BAC Tower}\end{array}$$

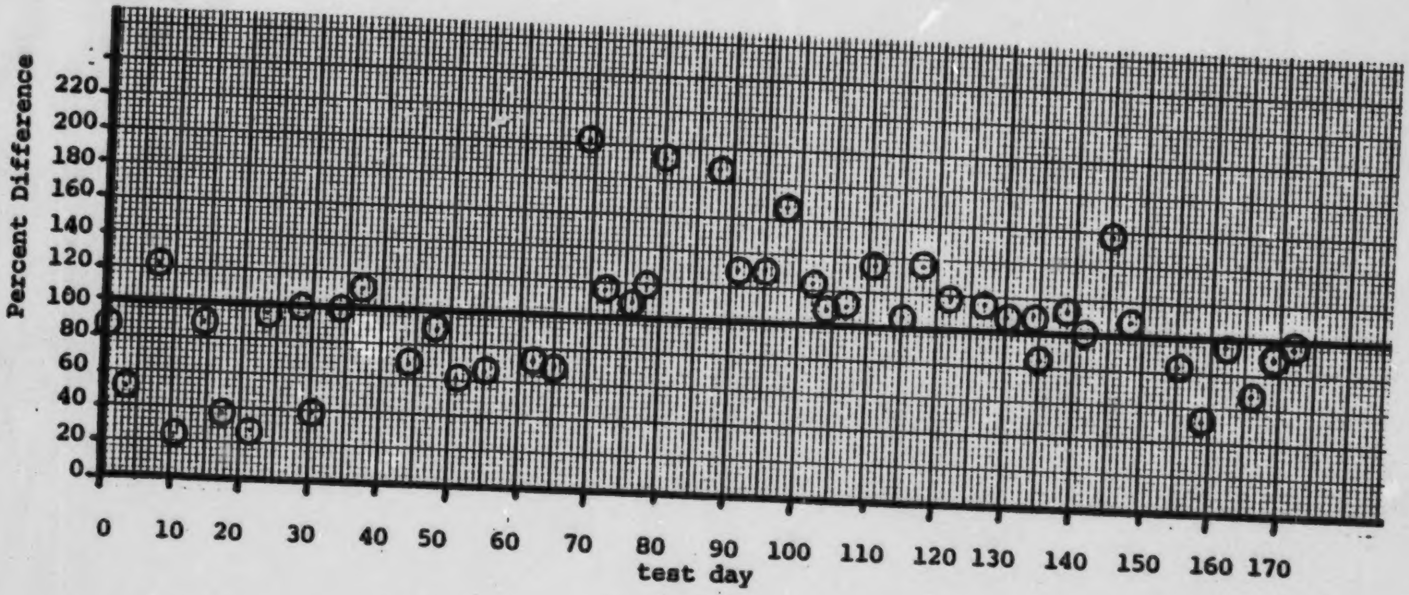


Figure 49. THMFP effluent from 10 ft. of ozone-BAC tower compared with THMFP effluent from 10 ft. of nonozone-BAC tower.

day 122 to day 172. In the first zone, the ozone-BAC system removed more THMFP, despite the fact that it received 13 percent more THMFP. In the second zone (day 65 to day 122), at all three bed depths, the ozone-BAC system passed much more THMFP than the nonozone-BAC system. In the third zone (122 days to 172 days), both systems responded alike. These results are summarized in Table 24.

## TABLE 24

## COMPARISON OF THMFP REMOVAL BY THE OZONE-BAC AND NONOZONE-BAC SYSTEMS (PS 2)

$$\text{Percent difference for each bed depth} = \frac{\text{THMFP in effluent from ozonated-BAC system}}{\text{THMFP in effluent from nonozonated-BAC system}} \times 100$$

AVERAGE VALUE

| Bed Depth | Initial Start-up To Day 65 | Day 65 To Day 122 | Day 122 To Day 172 | Total Test Period 172 Days |
|---|---|---|---|---|
| 2.5 Ft. | 97 | 173 | 98 | 122 |
| 5 Ft. | 85 | 151 | 98 | 121 |
| 10 Ft. | 73 | 137 | 100 | 102 |

If we compare the two systems for the first 65 days, the ozone-BAC system allowed passage of 97, 85 and 73 percent as much THMFP as the nonozone-BAC system for 2.5, 5 and 10 ft. of bed depth, respectively. From test day 65 to 122, the ozone-BAC system allowed passage of much more THMFP than the nonozone-BAC system (173, 151 and 137 percent, respectively, for the three bed depths). From test day 122 to the end of the test period (172 days), both systems performed almost identically, allowing the same passage. When compared over the full 172-day test period, the ozone-BAC system allowed 122, 121 and 102 percent passage of THMFP compared with the nonozone-BAC system for the 2.5, 5 and 10 ft. bed depths, respectively.

### Comparison of Ozone and Nonozone Systems for PS 1 and PS 2

In PS 1, the BAC towers in both the ozone-BAC and nonozone-BAC systems were anearobic from test day 0 to test day 98; they were then made aerobic by the addition of oxygen from test day 98 to the end of the test period at day 160. In PS 2, both towers were aerobic from day 0 to the end of the test period, day 172. It would be desirable to compare THMFP and TOC removal in the two studies, determining whether or not an anaerobic system differs from an aerobic system. It would also be desirable to compare removal rates for the two studies based on any other factors of interests.

The performance of TOC and THMFP removal in the two pilot studies can be judged by comparing accumulated influent and effluent results. The THMFP results for both studies are shown in Table 25. TOC results are shown in Table 26. These results were obtained by integrating the area under each influent and effluent curve. We should also consider in this comparison of pilot studies the major differences shown in Table 26. We should point out that there are slight differences in the calculated data on accumulated THMFP and TOC influent and effluent values when calculated from average THMFP and TOC values versus integration of each curve. The integration method would produce the more accurate results.

In Table 25, the accumulated THMFP influent to the nonozone-BAC system and to the ozone-BAC system is shown for both studies. The accumulated effluent from each system is also shown. In PS 1, bed life based on Criterion I for 10 ft. of carbon was 9 days for the nonozone-BAC system and 25 days for the ozone-BAC system. In PS 2, the corresponding days were 19 and 44. These four time periods in days were selected for comparison. In the PS 2 data, we also selected the 160 day time period for comparison with the 160 day total test period time in PS 1.

In Table 26, the accumulated TOC influent and effluent data are shown at 29, 37, 48 and 65 day time periods, based on the Criterion I bed life TOC breakthrough data. The 160 day time period is also shown.

From the data in Tables 25 and 26, comparison can be made of the performance of each BAC tower based on its own influent level, shown by single ( ). A comparison of percent removal by each system as a whole is shown by triple ((( ))). In Table 25, the double (( )) indicates the increased loading factor of THMFP entering the ozone-BAC system. In Table 25, we can also see the actual weight removed. In Table 26, the double (( )) indicates the increased loading factor of TOC entering the nonozone-BAC system.

Care should be taken not to overspeculate or conclude from these data. Many factors influence the removal rate. We showed in Refs. 1, 2 and 3 that the adsorptive capacity of GAC is dependent on influent concentration increasing as the concentration increases. We should also consider that during the time periods associated with Criterion I bed life, we are comparing removal results before reaching the pseudo-steady-state portion of the breakthrough curve. At the end of the test time period, we are comparing results over the entire breakthrough curve. We must also consider that when we compare THMFP removal, THMFP is only a small part of the overall TOC concentration level, and the effect that each has upon the other as far as GAC adsorption is concerned is unknown.

We have tried repeatedly to extract trends which might lead to conclusions based on the data in Tables 25 and 26, each time to be frustrated by the unknowns mentioned above. For this reason, we only present conclusions based on percent THMFP and TOC removed by the ozone system based on the influent to the nonozone system. That is, we are comparing the nonozone-BAC system as a whole with the ozone-BAC system as a whole. We will not look at the individual BAC tower performance separately. The data are there if anyone wishes to do so. Table 25 shows that in PS 1, the ozone-BAC system removed a

## TABLE 25

### ACCUMULATED THMFP (GRAMS) IN INFLUENT AND EFFLUENT FROM OZONE-BAC AND NONOZONE-BAC SYSTEMS IN PS 1 and PS 2

|  | ACCUMULATED RUN DAYS |  |  |  |  |  |
|---|---|---|---|---|---|---|
| Item | 9 | 19 | 25 | 44 | 160 | 172 |
| PS 1 SYSTEM |  |  |  |  |  |  |
| Nonozone influent | 496 | 1075 | 1454 | 3008 | 9654 |  |
| Nonozone effluent | 34(93) | 269(75) | 403(72) | 975(68) | 6192(36) |  |
| removed = | 462 | 806 | 1051 | 2033 | 3462 |  |
| Ozone influent | 605((1.22)) | 1160((1.08)) | 1546((1.06)) | 3092((1.03)) | 9982((1.03)) |  |
| Ozone effluent | 25(96)(((95))) | 50(96)(((95))) | 76(95)(((95))) | 261(92)(((91))) | 5352(46)(((45))) |  |
| removed = | 580 | 1110 | 1470 | 2831 | 4630 |  |
| PS 2 SYSTEM |  |  |  |  |  |  |
| Nonozone influent | 1017 | 1874 | 2353 | 4672 | 13948 | 14502 |
| Nonozone effluent | 143(86) | 412(78) | 571(76) | 1487(68) | 6755(52) | 7226(50) |
| removed = | 874 | 1462 | 1782 | 3185 | 7193 |  |
| Ozone influent | 849((0.84)) | 1437((0.76)) | 2638((1.12)) | 6050((1.30)) | 15889((1.14)) | 16460((1.14)) |
| Ozone effluent | 109(87)(((89))) | 227(84)(((88))) | 302(88)(((87))) | 1008(83)(((78))) | 6428(59)(((54))) | 6814(59)(((53))) |
| removed = | 740 | 1210 | 2336 | 5042 | 9461 |  |

( ) Percent removed by each system

(( )) THMFP influent to the ozone system divided by THMFP influent to the nonozone system

((( ))) Percent removed by the ozone system based on the influent to the nonozone system

## TABLE 26

## ACCUMULATED TOC (GRAMS) IN INFLUENT AND EFFLUENT FROM OZONE-BAC AND NONOZONE-BAC SYSTEMS IN PS 1 and PS 2

|  | ACCUMULATED RUN DAYS |  |  |  |  |  |
|---|---|---|---|---|---|---|
| Item | 29 | 37 | 48 | 65 | 160 | 172 |
| PS 1 SYSTEM |  |  |  |  |  |  |
| Nonozone influent | 26380((1.19)) | 33553((1.16)) | 43519((1.17)) | 60910((1.17)) | 164330((1.17)) |  |
| Nonozone effluent | 5713(78) | 9073(73) | 14366(67) | 22600(63) | 89894(45) |  |
| removed = | 20667 | 24480 | 29153 | 38310 | 74436 |  |
| Ozone influent | 22096 | 28649 | 37302 | 52172 | 140974 |  |
| Ozone effluent | 2100(90)(((92))) | 3613(87)(((89))) | 6721(82)(((85))) | 13106(75)(((78))) | 59481(58)(((64))) |  |
| removed = | 19996 | 25036 | 30581 | 39066 | 81493 |  |
| PS 2 SYSTEM |  |  |  |  |  |  |
| Nonozone influent | 29657((1.07)) | 37302((1.08)) | 46123((1.07)) | 59313((1.07)) | 145679((1.08)) | 157777((1.08))) |
| Nonozone effluent | 5461(82) | 8317(78) | 13190(71) | 21003(65) | 83845(42) | 93843(40) |
| removed = | 24196 | 28985 | 32933 | 38310 | 61834 |  |
| Ozone influent | 27808 | 34614 | 43015 | 55365 | 135346 | 146435 |
| Ozone effluent | 3025(89)(((90))) | 5125(85)(((86))) | 8233(81)(((82))) | 14198(74)(((76))) | 60238(55)(((59))) | 674[illegible]3(54)(((57))) |
| removed = | 24783 | 29489 | 34782 | 41167 | 75108 |  |

( ) Percent removed by each system

(( )) TOC influent to the ozone system divided by TOC influent to the non-ozone system

((( ))) Percent removed by the ozone system based on the influent to the non-ozone system higher percentage of THMFP than the nonozone-BAC system for all time periods. After 160 test days, the ozone-BAC system removed 45 percent of the THMFP entering the nonozone-BAC system which removed 36 percent. In PS 2, the ozone-BAC system removed a higher percentage of THMFP than the nonozone-BAC system for all time periods. At the 160-test day period, the ozone-BAC system removed 54 percent of the THMFP entering the nonozone-BAC system which removed 52 percent. In PS 1, the improvement was less for all time periods compared with PS 2, however, we cannot conclude that this was the result of a change from aerobic to anerobic conditions. Changes in THMFP and TOC loading for each ED and the conversion of TOC substances to THMFP substances by absorbed oxygen in PS 2 and not in PS 1 undoubtedly influence the results.

In Table 25, it should be noted that for both studies in most time periods, a higher concentration of THMFP entered the ozone-BAC tower than entered the nonozone-BAC tower. Also, the amount of THMFP in grams removed increased with the increase of THMFP influent. This is expected since the adsorptive capacity of GAC increases as the concentration increases. In Table 26, note that in all cases the nonozone-BAC tower always received more TOC than the ozone-BAC tower. However, more TOC in grams was always removed by the ozone-BAC tower. This is contrary to our previous statement that the adsorptive capacity of GAC increases as the concentration increases. When data appear to be contradictory or out of place, a search is usually made for an explanation.

From Table 21, we observe that the average TOC level in the clearwell water in PS 1 was 7.7 ppm over the entire test period, and in PS 2, the average was 6.77 ppm. However, in Table 26, we observe that the actual accumulated TOC loading was slightly higher in the first study than in the second to test day 48. The accumulated TOC loading to test day 65 was almost the same in both studies. At 160 days, the accumulated loading in PS 1 was considerably higher than in PS 2 (1.13 times higher). This change in TOC loading from day 0 to day 65 and from day 65 to day 100 should be considered in reaching any conclusions. In Table 26, we observe very little difference between the studies in TOC removal for day 0 to day 65. At test day 65, with the TOC-accumulated loadings almost equal, we observe almost the same removal rates. At test day 160, with 1.13 times the loading in PS 1, we observe higher removal rates in PS 1 than in PS 2. This would be expected since the adsorptive capacity of GAC increases as the concentration increases. Based on TOC removal, it might appear that aerobic and anaerobic conditions had essentially the same effect on the removal rate. However, it would still be best not to make this conclusion, but only keep it in mind.

It was stated earlier that comparisons of PS 1 and PS 2 from Tables 25 and 26 suffered from the fact that the removal rate of TOC and THMFP was being compared from day 0 to the end of the pre-pseudo-steady-state region of the breakthrough curve, with the removal rate at test day 160 for the whole breakthrough curve.

The data from Tables 25 and 26 can be considered in another way. We can also compare PS 1 and PS 2 performance based on the separate performance for each of the two breakthrough zones. Accumulated values for THMFP and TOC, for their respective pseudo-steady-state zones, are shown in Table 27. Once again, we must be careful in drawing conclusions. We might look at the ratio

## TABLE 27

## ACCUMULATED TOC AND THMFP INFLUENT AND EFFLUENT FROM OZONE-BAC AND NONOZONE-BAC SYSTEMS IN PS 1 AND PS 2 FOR PSEUDO-STEADY-STATE PORTION OF BREAKTHROUGH CURVE

| Item | THMFP (Grams) Day 44 To Day 160 | TOC (Grams) Day 65 To Day 160 |
|---|---|---|
| PS 1 SYSTEM | | |
| Nonozone influent | 6646 | 103420((1.17)) |
| Nonozone effluent | 5217(21) | 67294(35) |
| removed = | 1429 | 36126 |
| Ozone influent | 6890((1.04)) | 88802 |
| Ozone effluent | 5091(26)(((23))) | 46375(48)(((55))) |
| removed = | 1799 | 42427 |
| PS 2 SYSTEM | | |
| Nonozone influent | 9276 | 86366((1.08)) |
| Nonozone effluent | 5268(43) | 62842(27) |
| removed = | 4088 | 23524 |
| Ozone influent | 9839((1.06)) | 79981 |
| Ozone effluent | 5420(45)(((42))) | 46040(42)(((47))) |
| removed = | 4419 | 33941 |

( ) Percent removed by each system

(( )) THMFP influent to the ozone system divided by THMFP influent to the nonozone system

((( ))) Percent removed by the ozone system based on the influent to the nonozone system

## TABLE 28

## RATIO OF THMFP AND TOC REMOVAL FOR PS 1 AND PS 2 FOR THE TWO ZONES OF THE BREAKTHROUGH CURVE

| | THMFP |
|---|---|
| Pilot Study | Day 0 To Day 44 |
| PS 1 | $\frac{\text{ozone-BAC system (((91))) from Table 88}}{\text{nonozone-BAC system (68) from Table 88}} = 1.34$ |
| PS 2 | $\frac{(((78)))}{(68)} = 1.15$ |
| | Day 44 To Day 160 |
| PS 1 | $\frac{\text{ozone-BAC system (((23))) from Table 90}}{\text{nonozone-BAC system (21) from Table 90}} = 1.10$ |
| PS 2 | $\frac{(((42)))}{(43)} = 0.98$ |

| | TOC |
|---|---|
| | Day 0 To Day 65 |
| PS 1 | $\frac{\text{(((78))) from Table 89}}{\text{(63) from Table 89}} = 1.24$ |
| PS 2 | $\frac{(((76)))}{(65)} = 1.17$ |
| | Day 65 To Day 160 |
| PS 1 | $\frac{\text{(((55))) from Table 90}}{\text{(35) from Table 90}} = 1.57$ |
| PS 2 | $\frac{(((47)))}{(27)} = 1.74$ |

of performance for THMFP and TOC removal for the two zones of the breakthrough curve. In Table 28, we show the ratio of performance for each whole system for the two zones of the breakthrough curve.

Considering THMFP results for PS 1 in Table 27, we observe that from day 0 to day 44, the ozone-BAC system as a unit removed 91 percent of the THMFP (based on the level entering the nonozone-BAC system) compared with 68 percent removal by the nonozone-BAC system as a unit. The ratio of performance of the two systems is 1.34 (91/68=1.34). From day 44 to day 160, the ozone-BAC system removed 23 percent of the THMFP entering compared with 21 percent for the nonozone-BAC system, resulting in a ratio of performance of 1.10 (23/21= 1.10). During this pre-pseudo-steady-state portion of the breakthrough curve time zone, the performance of the ozone-BAC system was considerably better than the nonozone-BAC system—91 versus 68 percent removal. During the pseudo-steady-state time zone, the performance of the two systems was quite close, 23 percent versus 21 percent. The ratio of performance went down, 1.34 versus 1.10. It is tempting to try to conclude something from these data regarding THMFP removal by adsorption versus removal by bacteria consumption in the two zones, but too many unknown factors make this impossible. We should only conclude that the THMFP removal rate was much higher in the pre-pseudo-steady-state zone of the breakthrough curve compared with the pseudo-steady-state zone for both the ozone-BAC system and the nonozone-BAC system. Also, the ratio of percent removed by the two systems (percent THMFP removed by the ozone-BAC system divided by the percent removed by the nonozone-BAC system) was much higher in the first zone compared with the second zone (91/68 percent = 1.34) from day 0 to day 44, and it was 23/21 percent = 1.10 from day 44 to day 160 for PS 1. This conclusion was confirmed in PS 2 with values of 78/68 percent = 1.15 and 42/43 percent = 0.98.

TOC removal performance for the two zones can be compared from the data in Table 28. In both pilot studies, the ratio of TOC removal performance increased from the pre-pseudo-steady-state zone to the pseudo-steady-state zone, which is the reverse found with THMFP data. Once again, it is probably unwise to try to conclude anything regarding TOC removal by GAC adsorption versus bacteria consumption in the two zones.

We should only conclude that the TOC removal rate was much higher in the pre-pseudo-steady-state zone of the breakthrough curve compared with the pseudo-steady-state zone for both the ozone-BAC system and the nonozone-BAC system. Also, the ratio of percent removed by the two systems (percent TOC removed by the ozone-BAC system divided by the percent removed by the nonozone-BAC system) was much higher in the pseudo-steady-state zone (78/63 percent = 1.24 from day 0 to day 65 and 55/35 percent = 1.57 from day 65 to day 160 for PS 1, and 76/65 percent = 1.17 and 47/27 =1.74 for PS 2).

We cannot make a conclusion regarding the removal of THMFP or TOC based on the anaerobic conditions in the beginning of PS 1 compared with the aerobic condition in PS 2.

Up to now in this report we have avoided, for reasons stated, a comparison of the performance of the BAC tower receiving ozonated water versus the BAC tower receiving nonozonated water. If a direct comparison is to be made, both towers would have to be receiving at least the same influent TOC concentration—that is, the same averaged mg/L of TOC. Using Figures 14 and 46, we can select a common accumulated TOC influent for both pilot studies (146,000 grams in 160 days was selected). We can then read from each curve the corresponding accumulated TOC that would be removed. The results obtained appear in Table 29.

### TABLE 29

### ACCUMULATED GRAMS OF TOC REMOVED IN 160 DAYS AT A COMMON 146,000 ACCUMULATED TOC INFLUENT LEVEL

| PS 1 (Fig. 14) | 2.5 Ft. | | 5 Ft. | | 10 Ft. | |
|---|---|---|---|---|---|---|
| Ozone-BAC | 50,500 | (1.39) | 66,000 | (1.32) | 82,500 | (1.23) |
| Nonozone-BAC | 36,300 | | 50,000 | | 67,000 | |
| PS 2 (Fig. 46) | | | | | | |
| Ozone-BAC | 43,500 | (1.34) | 61,000 | (1.31) | 76,000 | (1.14) |
| Nonozone-BAC | 32,500 | | 46,500 | | 66,500 | |

The values above in parentheses are the ratios of the ozone-BAC value divided by the nonozone-BAC value.

These results tell us something about the effect that ozonation of our water (in the range of an absorbed ozone dose of 11.3 to 14.5 mg/L) has on the removal rate of TOC by BAC towers receiving the same total influent TOC level, but at different mg/L concentration. The results indicate that in PS 1, at a common influent level of TOC of 146,000 grams, the TOC removed by 2.5, 5 and 10 ft. of BAC tower was 1.39, 1.32 and 1.23 times as much, respectivley, when the water was ozonated. In PS 2, the respective values were 1.34, 1.31 and 1.14. Thus ozonation does result in more removal of TOC by a BAC tower. However, the common influent TOC level is still at a different concentration of TOC in mg/L. We still need some way of predicting what would happen if the influent mg/L were identical. Ideally, we could perform an experiment in which, after ozonation at the desired absorbed ozone dose, the mg/L of TOC exactly equaled the TOC in a nonozonated feed. Lacking running the experiment, we still might be able to approximate the answer.

In Ref. 1, we showed that the adsorptive capacity of GAC for a given compound depended on influent concentration and increased as the concentration increased. We then showed that the adsorptive capacity of GAC for a given compound at saturation produced a linear relationship, at low concentration, when log adsorptive capacity was plotted versus log influent concentration. We then showed that this linear plot was useful in predicting what the adsorptive capacity would be at some concentration other than that which was tested and also, we could directly compare adsorptive capacity from one experiment to another at a common influent concentration. We admit that by using this procedure in this present case with TOC substances as the compound in question (and with many other factors in question), we are only performing an exercise that may or may not result in useful data. However, at least going through the exercise may assist someone who has data that could be handled in this way.

In Figure 50, for 160 days of testing at all three bed depths, we have plotted on log-log paper the grams of TOC removed by the BAC towers in PS 1 and PS 2 versus the corresponding TOC influent. On the X-axis, the total influent accumulated TOC figured in grams in 160 days represents a concentration in mg/L.

In Figure 50, we can extend the curves to intersect the mg/L of influent TOC resulting in an accumulated TOC loading of 146,000 grams. We can then read on the Y-axis the corresponding grams of TOC that would be removed at this influent concentration.

The results are shown in Figure 50. We hope that the results tell us something about the effect that ozonation of our water (in the range of an absorbed ozone dose of 11.3 to 14.5 mg/L) has on the removal rate of TOC by BAC towers receiving the same influent TOC level. The results show that at a common influent level of TOC of 146,000 grams in a period of 160 days, the amount of TOC removed by 2.5, 5 and 10 ft. of tower for ozonated versus nonozonated water would be (a) 50,500 compared with 29,000, (b) 66,000 compared with 42,000, and (c) 82,500 compared with 65,000, respectively. At 2.5, 5 and 10 ft., ozonation would result in the towers removing 1.74, 1.57 and 1.27 times as much TOC, respectively. These ratio values, as expected, are higher than the ratio values obtained from the curves in Figures 14 and 46. How close the values are to the true values that would be obtained by experimentation remains speculative.

Comparison of PS 1 and PS 2 Based on Bed Life in Days to Reach Criterion 1—

As stated previously, effective bed life can be based on the number of days to reach a breakthrough of 3 mg/L of TOC or 200 µg/L of THMFP (Criterion 1). Data based on this criterion are shown in Table 30. The plotted curves from which these data were obtained are identified by figure number.

TOC Comparison

Except for the 2.5 ft. data in Table 30, the days to reach breakthrough of 3 mg/L of TOC in PS 2 was considerably less than in PS 1. This was probably due to the higher TOC loading in PS 2 (see Table 26).

Another significant factor from Table 30 was the fact that in both studies, the ozone-BAC system gave longer bed life than the nonozone-BAC system. If we compare the 10 ft. bed data, in PS 1 the ozone system was 1.67 times longer, Grams of TOC removed at a common TOC concentration (mg/l) resulting in an accumulated TOC loading of 146,000 grams in 160 days.

| | 2.5 feet | | 5 feet | | 10 feet | |
|---|---|---|---|---|---|---|
| Ozone-BAC | 50,500 | | 66,000 | | 82,500 | |
| Non-ozone-BAC | 29,000 | (1.74) | 42,000 | (1.57) | 65,000 | (1.27) |

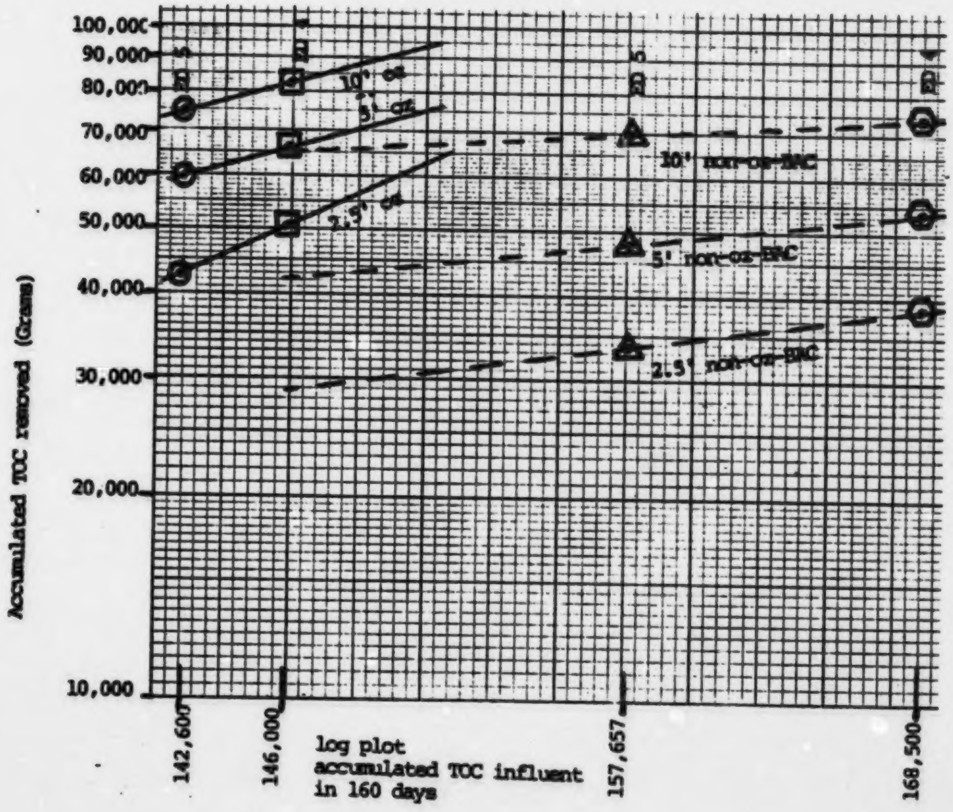


Figure 50. Log - Log plot of accumulated TOC removal versus accumulated TOC influent in 160 days (PS 1 and PS 2).

## TABLE 30

## BAC BED LIFE IN DAYS FOR PS 1 AND PS 2 BASED ON PASSAGE OF 3 mg/L OF TOC AND 200 µg/L OF THMFP

| Taken From | Pilot Study No. | System | THMFP<br>Bed Life In Days Based On Passage Of 200 µg/L Of THMFP<br>2.5 Ft. | <br><br>5 Ft. | <br><br>10 Ft. |
|---|---|---|---|---|---|
| Figure 111 | 1 | Nonozone-BAC | 1 | 19 | 19 |
| Figure 109 | 1 | Ozone-BAC | 10 | 24 | 44 |
| Figure 136 | 2 | Nonozone-BAC | 2 | 6 | 9 |
| Figure 137 | 2 | Ozone-BAC | 4 | 8 | 25 |

| Taken From | Pilot Study No. | System | TOC<br>Bed Life In Days Based On Passage Of 3 mg/L Of TOC<br>2.5 Ft. | <br><br>5 Ft. | <br><br>10 Ft. |
|---|---|---|---|---|---|
| Figure 103 | 1 | Nonozone-BAC | 17 | 26 | 29 |
| Figure 101 | 1 | Ozone-BAC | 23 | 38 | 48 |
| Figure 124 | 2 | Nonozone-BAC | 5 | 7 | 37 |
| Figure 125 | 2 | Ozone-BAC | 5 | 37 | 65 |

and in PS 2, it was 1.76 times longer. Longer times for the ozone system were also observed for 2.5 ft. and 5 ft. of bed depth. Since the BAC tower in the ozone system received less TOC (destroyed by ozonation in the ozone contactor), longer bed life would be expected.

We cannot really determine for either the ozone or the nonozone system how much contribution to the increased bed life in Table 26 was due to reduction of TOC by bacteria in the BAC towers and how much was due to the lower TOC influent.

THMFP Comparison

The effective bed life, based on breakthrough of 200 μg/L of THMFP, is shown in Table 30. The plotted curves from which the bed life was determined are identified by figure number. In Table 30, it is apparent, as with TOC, that the ozone-BAC system gave a longer bed life than the nonozone-BAC system. For example, with 10 ft. of bed depth, in PS 1 the bed life was 19 and 44 days, respectively, for the nonozone and ozone systems--an increase of 2.32 times. In PS 2, the bed life was 9 and 25 days, an increase of 2.78 times. The shorter bed life in PS 2 might again be explained by the higher TOC loading in PS 2 (the GAC not seeing the higher THMFP as a separate group of the overall TOC substances). Again, we cannot really determine the contribution associated with adsorption versus bacteria removal.

Carbon Use Rate for PS 1 and PS 2--

In PS 1 and PS 2, the weight of GAC in each BAC tower was 2,050 pounds. The carbon use rates for 10 ft. of bed depth (pounds of carbon to treat 1 million gallons of water for THMFP removal based on Criterion 1) are shown in in Table 31.

TABLE 31

POUNDS OF GAC (10 FT. OF BED DEPTH) REQUIRED TO TREAT 1 MILLION GALLONS OF WATER FOR THMFP REMOVAL BASED ON CRITERION 1 (PS 1 AND PS 2)

| Item | Bed Life In Days | Pounds Of GAC To Treat 1 Million Gallons Of Water |
|---|---|---|
| PS 1 SYSTEM | | |
| Nonozone-BAC | 19 | 2,997 |
| Ozone-BAC | 44 | 1,294 |
| PS 2 SYSTEM | | |
| Nonozone-BAC | 9 | 6,327 |
| Ozone-BAC | 25 | 2,278 |

The bench-scale research project (Ref.1) and this research project sought to lower the level of TTHM reaching the consumer's tap by removing THMFP substances at the drinking water treatment plant, and still maintain a free chlorine level of approximately 2.5 ppm in the finished water leaving the plant for continued disinfection in the distribution system. In Ref.1, GAC was the best adsorbent found for THMFP removal. Ten feet of Filtrasorb-400 on finished water, followed by rechlorination to 2.5 ppm of free chlorine, resulted in a bed life of 81 days (based on the regrowth of TTHM to 100 µg/L in 2 days of retention time in sealed vials, simulating 2 days of retention time in the distribution system). Since the bed life was short, this pilot plant project was designed to study the European water treatment process with hopes that on our water, the effective bed life would be greatly extended.

In Ref.1, with a bed life of 81 days on finished water, the carbon use rate per million gallons of water was 797 pounds.

For comparison with the data in Table 21 in this report, the average level of TOC and THMFP in the finished water entering the BAC column in Ref. 1 was 5.4 ppm and 434 µg/L, respectively. We cannot predict what the results would be using 10 ft. of BAC on the finished water at the Preston plant during the time periods associated with PS 1 and PS 2. We cannot conclusively say that on our water it would be better to treat finished water with 10 ft. of BAC or to treat ozonated, lime-softened water with 10 ft. of BAC. However, as the level of TOC increases, we would expect the bed life on finished water to decrease and be less than 81 days. We can conclude that on our water, removal of THMFP by 10 ft. of BAC, either on finished water or on ozonated, lime-softened water, does not (because of the short bed life in either case) appear to be a practical method of reducing TTHM levels reaching the consumer.

## Ozone Profile

Over the 172-day test period, with a water flow rate of 25 gpm through the MOC-BOC series ozone contactors, the average absorbed ozone dose was 14.5 mg/L. Analysis of the data generated indicates the effects of this single absorbed dosage rate on our water. A three-part experiment was designed to study the effects of increased dosage rates and the effects of pH.

For this work, one of the unused storage basins (as shown in Figure 31) was filled with lime-softened water directly from the lime-softener (pH 10). When the storage tank was filled, the water in the tank was circulated by a pump to ensure complete uniformity. This water, at a pH of 10, was then passed through the MOC-BOC series contactors at the usual rate of 25 gpm. Samples were taken of the influent water and water from the MOC and BOC. With no interruption or change in the ozone feed after sampling at the 25 gpm rate, the water flow through the system was reduced to 12.5 gpm. After sufficient time to ensure stability of the whole system at the new flow rate, sampling was repeated. At pH 10, this was repeated at a water flow rate of 6.25 gpm, and on one of the three complete runs, it was repeated at a flow rate of 3 gpm. After the pH 10 testing, again without interruption, the influent water was recarbonated to a pH of 7 and the water flow rate varied as above. The three separate test runs were made on September 23, 1981, October 29, 1981, and December 9, 1981. The data are presented in Tables 32 and 33.

### Effect of Water Flow Rate and pH on Ozone Profile—

In Table 32, we observe that as the water flow rate decreased, the percent transfer efficiency decreased. However, even though the percent transfer efficiency decreased, the absorbed ozone dose increased, because the effective contact time increased (given in Table 33). In general, the percent transfer efficiency was higher at all water flow rates for the pH 10 runs, resulting in higher absorbed ozone dosage.

### Effect of Absorbed Ozone Dosage and pH on TOC—

The TOC profile for the three sampling points is given in Table 32. Each complete test run required over 10 hours of continuous pumping from the storage tank. The TOC level of influent water for each water flow rate and pH was determined. Thus in Table 32 we have six replicates of influent TOC level, averaging 5.88 mg/L. The TOC level in the effluent from the BOC and the MOC is given, as well as the percent remaining based on the influent average level. These data are plotted in Figure 51. A separate graph is shown for each separate run. The average TOC influent level is shown on the "Y" axis by the "X" mark. The resulting TOC level is plotted at pH 10 and pH 7 at the corresponding absorbed ozone dose achieved by varying the water flow rate.

From these data, we conclude:

1) Up to an absorbed ozone dose level of approximately 45 mg/L, the reduction in TOC level was quite consistent for the pH range of 7 to 10.

2) For water tested in September, October, and December, respectively, absorbed ozone level required to destroy 1 mg of TOC (completely convert to $CO_2$) was 15.2, 16 and 20 mg/L, respectively.

3) Only in one test run, Run #II, was the water flow rate reduced to approximately 3 gpm resulting in absorbed ozone dose levels of 76 and 86 µg/L at pH 7 and pH 10, respectively. This flow rate was at the extreme lower limit we could reach with our pumps. Thus the actual flow rate could have varied somewhat throughout the test. In view of this, and with only one data point at the higher absorbed ozone dosage, we cannot conclude that the TOC reduction curve changed slope as the absorbed ozone dosage increased above approximately 45 mg/L. We can only conclude that as the absorbed dosage increased, we continuedto get a reduction in TOC.

### Effect of Absorbed Ozone Dosage and pH on THMFP—

THMFP data are presented in Table 32. Once again, we have at least six determinations of each test run period on the influent level of THMFP. The average value for each test run is shown. The variation in each set of data

# TABLE 32

## EFFECT OF ABSORBED OZONE DOSE AND pH ON TOC AND THMFP

Run #I (9/23/81)

| | | Influent to ozone contactors | | Effluent from MOC | | | Effluent from BOC | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | ozone | |
| gal/min | pH | TOC mg/L | THM FP ug/L | TOC mg/L | TOC % | THM FP ug/L | TOC mg/L | TOC % | THM FP ug/L | % Trans. Eff. | abs. dose mg/L |
| 25 | 10 | 6.1 | 334 | 5.6 | 95 | 317 | 5.65 | 96 | 341 | 91 | 10.9 |
| 12.5 | 10 | 5.8 | 331 | 4.35 | 74 | 352 | 3.8 | 65 | 428 | 84 | 22.9 |
| 6.25 | 10 | 5.75 | 251 | 2.45 | 42 | 279 | 2.1 | 36 | 386 | 68 | 41.2 |
| 25 | 7 | 5.95 | 326 | 5.65 | 96 | 298 | 5.65 | 96 | 304 | 63 | 8.8 |
| 12.5 | 7 | 5.85 | 291 | 4.35 | 74 | 336 | 4.3 | 74 | 414 | 56 | 18.3 |
| 6.25 | 7 | 5.7 | 413 | 3.89 | 66 | 280 | 2.5 | 43 | 382 | 52 | 44.8 |
| average | | 5.88 | 324 | | | | | | 376 (116%) | | |

Run #II (10/29/81)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | 10 | 7.66 | 422 | 6.58 | 87 | 436 | 6.62 | 87 | 440 | 86 | 9.5 |
| 12.5 | 10 | 7.73 | 321 | 6.35 | 84 | 404 | 6.46 | 85 | 421 | 82 | 17.4 |
| 6.25 | 10 | 7.24 | 355 | 5.81 | 77 | 373 | 5.5 | 72 | 385 | 77 | 32.8 |
| 3 | 10 | 7.89 | 207 | 5.08 | 67 | 276 | 4.6 | 61 | 278 | 51 | 86.1 |
| 25 | 7 | 7.77 | 404 | 7.14 | 94 | 427 | 6.74 | 89 | 437 | 70 | 10.4 |
| 12.5 | 7 | 7.45 | 383 | 6.59 | 87 | 364 | 6.35 | 84 | 363 | 54 | 18.4 |
| 6.25 | 7 | 7.23 | 345 | 6.08 | 84 | 341 | 5.69 | 75 | 358 | 46 | 32 |
| 3 | 7 | 7.79 | 371 | 5.93 | 78 | 329 | 5.76 | 72 | 345 | 36 | 76.7 |
| average | | 7.6 | 351 | | | | | | 401 for 25, 12.5 and 6.25 (114%) | | |

Run #III (12/09/81)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | 10 | 6.66 | 309 | 6.34 | 93 | 336 | 6.17 | 91 | 363 | 88 | 8.39 |
| 12.5 | 10 | 6.74 | 298 | 5.84 | 86 | 302 | 5.7 | 84 | 354 | 83 | 18.4 |
| 6.25 | 10 | 6.98 | 414 | 5.44 | 80 | 398 | 5.14 | 76 | 339 | 77 | 30.2 |
| 25 | 7 | 6.60 | 407 | 6.18 | 91 | 402 | 6.11 | 90 | 401 | 75 | 8.2 |
| 12.5 | 7 | 6.67 | 257 | 6.09 | 90 | 298 | 6.04 | 89 | 358 | 56 | 16.6 |
| 6.25 | 7 | 7.07 | 346 | 6.04 | 89 | 341 | 5.68 | 84 | 380 | 36 | 26.1 |
| average | | 6.78 | 339 | | | | | | 367 (108%) | | |

## TABLE 33

## FREE OZONE RESIDUAL PROFILE IN MOC AND BOC

### Run #I (9/23/81)

| | | MOC Effluent | | | | BOC Effluent | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | ozone | |
| gal/min | pH | Contact time min. | Mg/L free ozone | Contact time 5 min. 2.8 + 2.2 | Mg/L free ozone | Contact time min. | Mg/L free ozone | % trans. | Abs. dose mg/L |
| 25 | 10 | 2.8 | 0 | x | 0 | 11.3 | 0 | 91 | 10.9 |
| 12.5 | 10 | 5.6 | 0.45 | | | 22.6 | 0 | 84 | 22.9 |
| 6.25 | 10 | 11.2 | 1.12 | | | 45.2 | 0 | 68 | 41.2 |
| 25 | 7 | 2.8 | 1.68 | x | 0.36 | 11.3 | 0 | 63 | 8.8 |
| 12.5 | 7 | 5.6 | 2.54 | | | 22.6 | 0.22 | 56 | 18.3 |
| 6.25 | 7 | 11.2 | 3.08 | | | 45.2 | 0.51 | 52 | 44.8 |

### Run #II (10/29/81)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 25 | 10 | 2.8 | 0 | x | 0 | 11.3 | 0 | 86 | 9.5 |
| 12.5 | 10 | 5.6 | 0.15 | | | 22.6 | 0 | 82 | 17.4 |
| 6.25 | 10 | 11.2 | 0.29 | | | 45.2 | 0 | 77 | 32.8 |
| 3 | 10 | 23.3 | 2.04 | | | 94.2 | 0.43 | 51 | 86.1 |
| 25 | 7 | 2.8 | 1.48 | x | 0.25 | 11.3 | 0.14 | 70 | 10.4 |
| 12.5 | 7 | 5.6 | 1.99 | | | 22.6 | 0.2 | 54 | 18.4 |
| 6.25 | 7 | 11.2 | 2.45 | | | 45.2 | 0.4 | 46 | 32 |
| 3 | 7 | 23.3 | 2.64 | | | 94.2 | 0.4 | 36 | 76.7 |

### Run #III (12/09/81)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 25 | 10 | 2.8 | 0 | x | 0 | 11.3 | 0 | 88 | 8.39 |
| 12.5 | 10 | 5.6 | 0.23 | | | 22.6 | 0 | 83 | 18.4 |
| 6.25 | 10 | 11.2 | 0.42 | | | 45.2 | 0 | 77 | 30.2 |
| 25 | 7 | 2.8 | 0.91 | x | 0.14 | 11.3 | 0 | 75 | 8.2 |
| 12.5 | 7 | 5.6 | 0.29 | | | 22.6 | 0.22 | 56 | 16.6 |
| 6.25 | 7 | 11.2 | 2.6 | | | 45.2 | 0.55 | 36 | 26.1 |

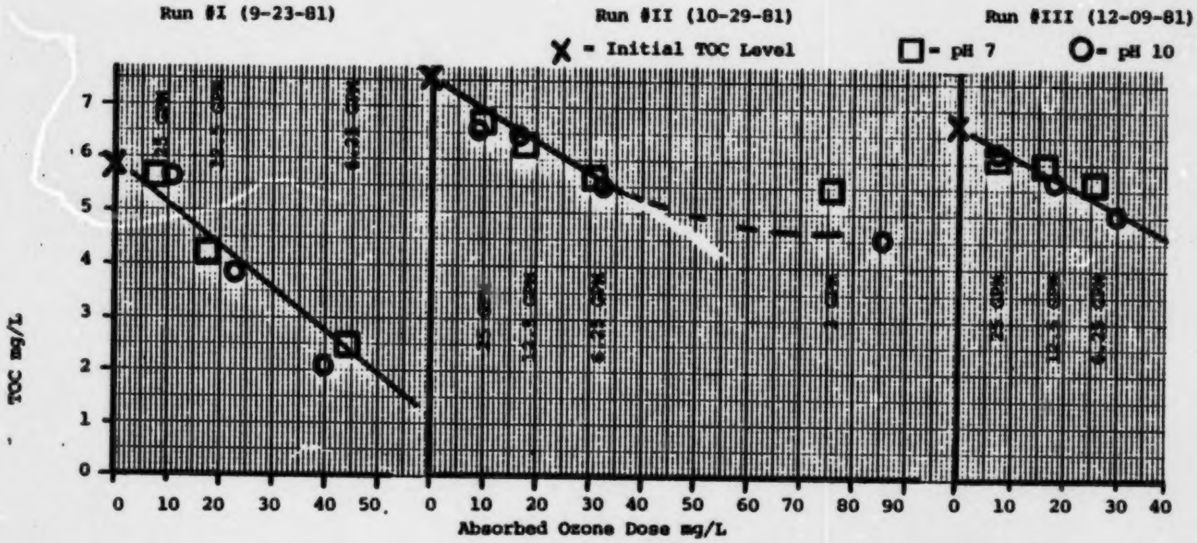


Figure 51. Effect of ozone dosage and pH on TOC removal.

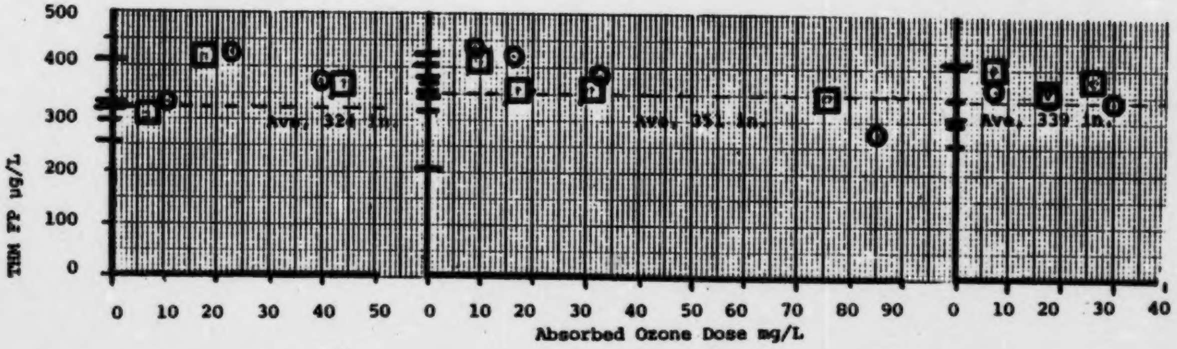


Figure 52. Effect of ozone dosage and pH on THMFP concentration.

is an indication of the analytical spread of the data. The THMFP data are plotted in Figure 52. The average THMFP value for each run is indicated as well as the individual data points (on the "Y" axis) making up this average.

From the data, we conclude:

1) Up to an absorbed ozone dose level of approximately 45 mg/L, the level of THMFP remains quite constant for the pH range of 7 to 10. There is a rise in the THMFP level over the average influent level. For the three separate runs, the increased values were 116, 114 and 108 percent, respectively .

2) In the one run where the absorbed ozone dose level was raised to approximately 76 and 86 mg/L for pH 7 and pH 10 respectively, we also observed a THMFP level well within the influent level spread. Even though the applied ozone dosage reduces the TOC level by as much as 64 percent, the THMFP level remained essentially the same, slightly higher than the initial influent level. Apparently, as TOC was destroyed (converted completely to $CO_2$), the TOC substances responsible for THM formation were either not destroyed, not destroyed at the same rate or new substances were continually formed at a rate resulting in an overall net uniform increase. A guess would be that THMFP substances were continuously destroyed, with new ones continuously forming, resulting in a uniform net increase.

### Free Ozone Residual—

The free ozone residual profile in the ozone contactors is shown in Table 33. No conclusions were drawn.

## Closed-Loop Stripping Analysis Profile

Our combined 5 years of research on water at the Preston plant (including other Dade County water treatment plants) in Ref. 1 and in this project has shown that other than the volatile chlorinated organics already present in the raw water from the wells and the THM's generated in the water treatment plant, the finished water from the Preston plant has a low concentration of organic compounds (see Tables 4 through 9 in Ref. 1 and Appendix Tables 1, 27, 42 and 57 in this report). This is illustrated by the use of the analytical method giving perhaps the greatest sensitivity. This method is the closed-loop stripping analysis (Refs. 42 and 43) followed by capillary electron capture detector (ECD) and flame ionization detector (FID). In PS 2, this method of analysis was used throughout the testing period on the following sampling points:

| | |
|---|---|
| Sample #3 | Water from the clearwell after recarbonation to pH 8.5, just before entering the nonozone-BAC tower and the ozone contactors. |
| #7 | Effluent from the MOC-BOC. |
| #C8-4 | Effluent from the 10 ft. bed depth ozone-BAC tower. |
| #C9 | Effluent water from the chlorine contact basins following the ozone-BAC tower (see Figure 11). Sufficient chlorine was added to obtain |

approximately a free chlorine level of 2.5 ppm after 1 hr of chlorine contact time.

#D8-4 Effluent from the 10 ft. bed depth nonozone-BAC tower.

#D9 Same as #C9, but following the nonozone-BAC tower.

Throughout the test period for PS 2, all samples were handled exactly the same. One half gallon of water sample was purged in the closed-loop stripping apparatus. The purged compounds were collected on the Grob activated charcoal trap. The trap was extracted with 10 µL of $CS_2$ and 2 µL of the extract was injected on the capilliary GC columns using the ECD and FID. All samples contained four or more internal standards as shown in Table 34.

TABLE 34

INTERNAL STANDARD CONCENTRATION FOR CLOSED LOOP SYSTEM ANALYSIS IN PS 2

| | Concentration For ECD And FID | |
|---|---|---|
| Straight Chain Internal Standard Compound | Nanograms In 2 µL Of 10 µL $CS_2$ - Extract | Concentration in ppt Of Purged Water Sample |
| Monochloro $C_6$ | 15.1 | 40 |
| Monochloro $C_8$ | 16 | 42 |
| Monochloro $C_{10}$ | 22.6 | 60 |
| Monochloro $C_{12}$ | 22.8 | 60 |
| Monochloro $C_{16}$ | 23.2 | 61 |
| Monochloro $C_{18}$ | 25.4 | 67 |

ECD and FID capillary chromatograms of the internal standards put through the full closed-loop analysis method and all chromatograms for all the sampling points throughout PS 2 were submitted to the EPA Project Officer in the final report. All ECD and FID chromatograms have arrows showing the capillary peaks for the internal standards. With both detectors, the internal standards show peaks from half full-scale to off-scale heights for concentrations from 40 to 67 ppt. We can relate the retention time of the internal standards to some actual compounds present in our water. Chlorobenzene has a retention time near the $C_6$ internal standard and dichlorobenzenes are near the $C_8$ compound. Dichloro PCB comes out near $C_{16}$. Peaks in the ECD and FID capillary chromatograms of the water samples with retention times up to the $C_8$ internal standards are in general the volatile chlorinated organics up to and including the dichlorobenzenes. Their concentration is high enough that all have been confirmed by GC/MS analysis. In general, the peaks beyond the $C_8$ internal standard are small, less than 1 ppb, which is too low for identification by GC/MS. The purpose of this closed-loop analysis profile in PS 2 was to show by chromatograms the existence of peaks both identifiable and unidentifiable by GC/MS in various water samples and their fate through the pilot plant stages. Only some typical chromatograms are shown in this report and some conclusions are presented. Figure 53 shows typical ECD and FID capillary chromatograms of the internal chloroalkane standards. Retention times for the standards gradually changed as the testing period progressed as a result of aging of the capillary columns.

In Figure 54, Chromatogram #3 shows large off-scale peaks before the $C_6$ standard for the volatile chlorinated compounds shown in Table 18. Chromatogram #7 shows the reduction of these compounds by ozone. Chromatogram C8-4 shows further reduction of the compounds early in the test by adsorption in the ozone-BAC tower (10 ft. bed depth). Figure 55 shows C8-4 later into the test run with an increased number of peaks as some of the volatile chlorinated compounds begin to break through the ozone-BAC tower. In Figure 55, Chromatogram C-9 shows the large increase in the number of peaks caused by chlorination of the ozone-BAC tower effluent (chlorinated to a free chlorine level of 2.5 ppm after 1 hour of chlorine contact time). The chlorinated compounds formed beyond the $C_6$ standard, while generally low in concentration (a few ppb or less), also generally remain unidentified. In Figure 56, D8-4 (the effluent from the nonozone-BAC tower) shows more peaks than C8-4 in Figure 54 (peaks reduced by ozone destruction of double-bond chlorinated compounds). D-9 and C-9, the chlorinated BAC tower effluents, are similar.

From all the ECD Chromatograms generated over the 172-day test period, we conclude:

The number of ECD peaks and the concentration levels of compounds present in the clearwell water in PS 2 are generally reduced by ozonation. Ozonation does not produce new compounds detected by the ECD. The 10 ft. deep BAC tower receiving ozonated water further reduces the number of ECD peaks and concentration involved. The number of ECD peaks and concentration involved gradually increase as compounds break through and reach saturation in the BAC tower effluent as the test period progresses. The number of ECD peaks and concentrations involved are greater in the effluent from the 10 ft. deep nonozone-BAC tower (not reduced by ozonation). After a BAC tower, rechlorination to 2.5 ppm of free chlorine (chlorine contact time of an hour) results in formation of additional chlorine compounds before the $C_6$ standard (triholomethanes, mono and dichlorobenzenes, etc.). Also, perhaps at least 50 additional chlorinated compounds are produced with molecular weights above the $C_6$ standard. While low in concentration, a few ppb or less, the

CHLOROALKANE STD

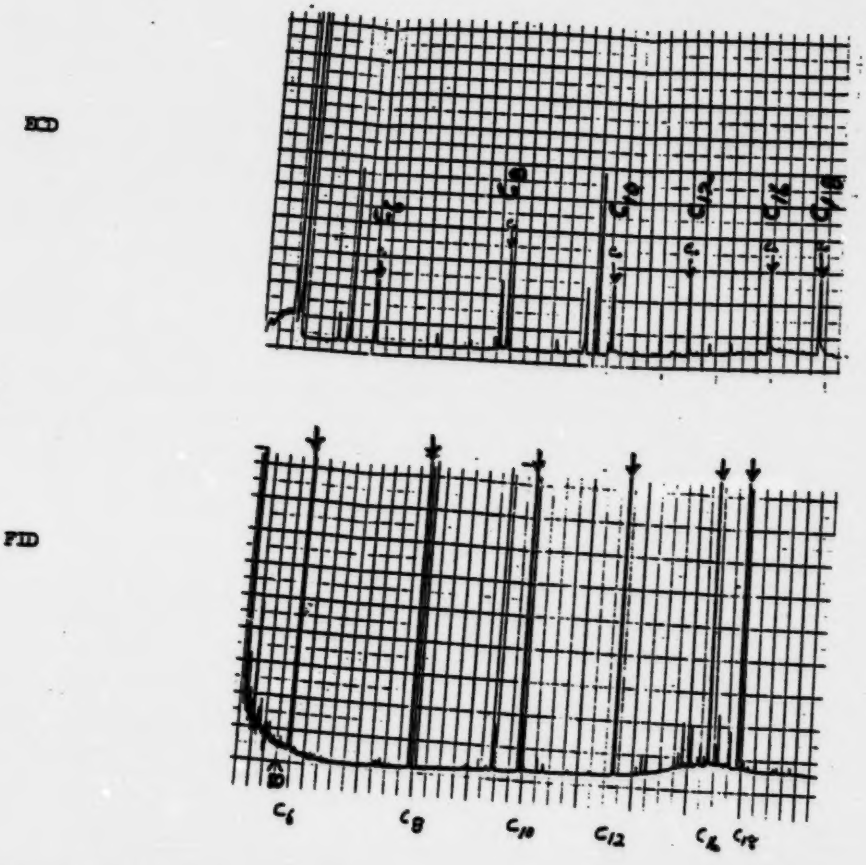


Figure 53. Internal chloralkane standards in closed-loop analysis.

ELECTRON CAPTURE DETECTOR
(CLSA)

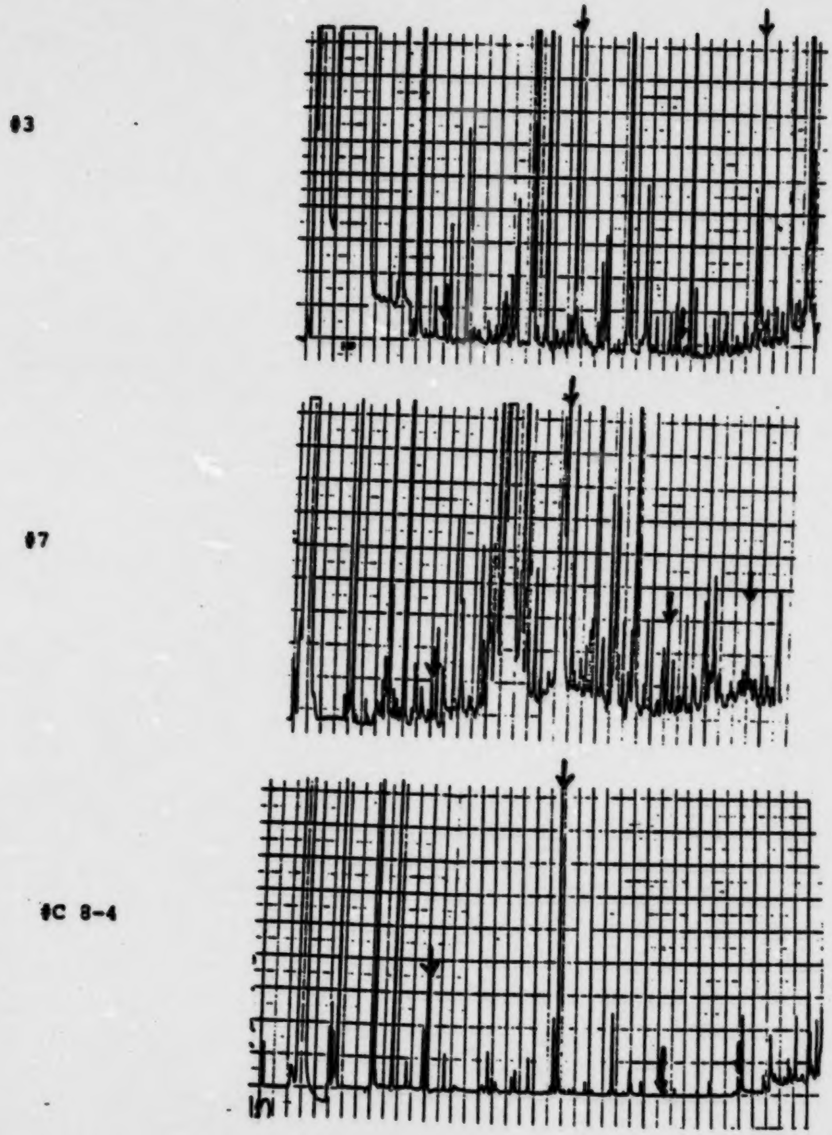


Figure 54. Closed-loop stripping analysis (capillary column ECD).

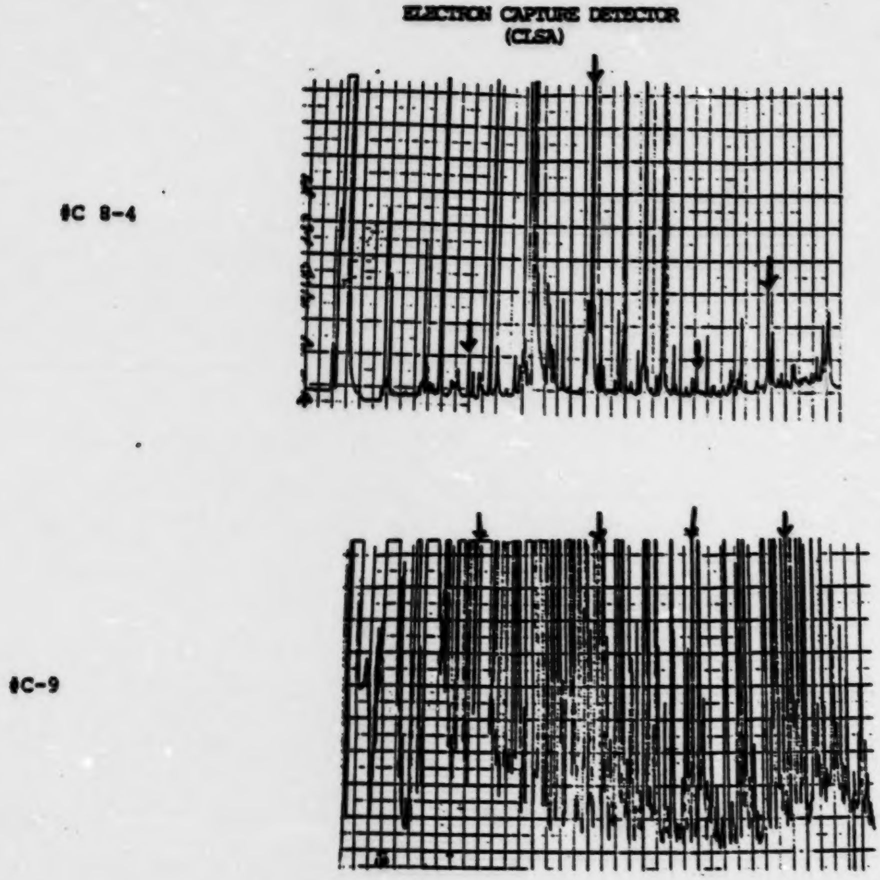


Figure 55. Closed-loop stripping analysis (capillary column ECD).

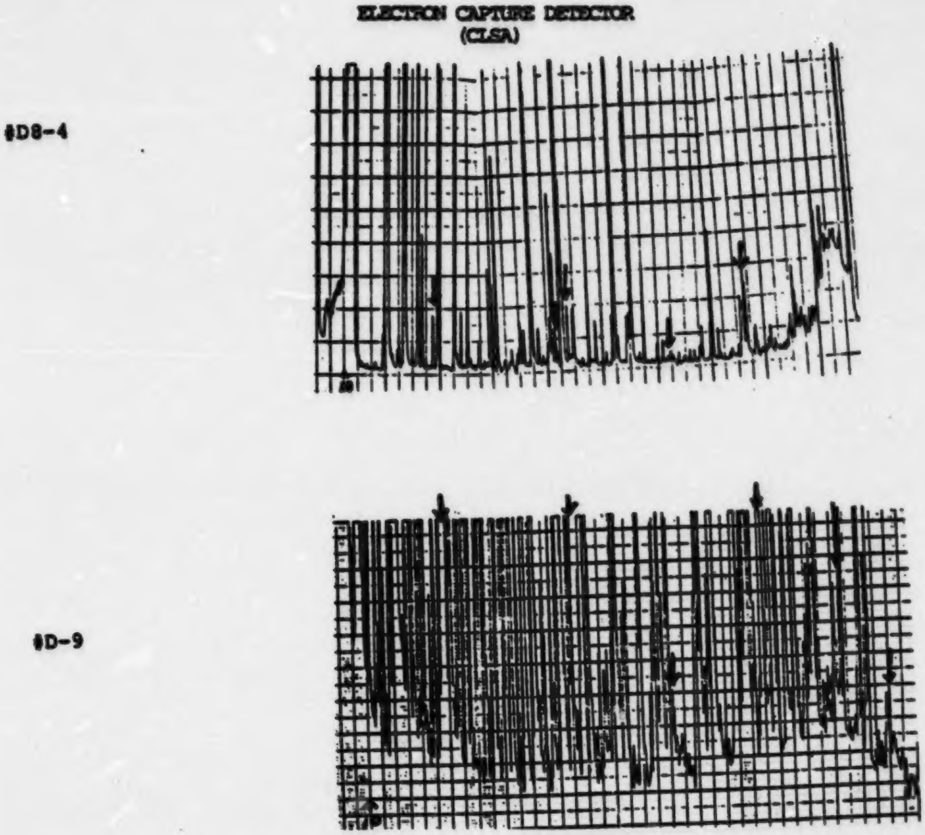


Figure 56. Closed-loop stripping analysis (capillary column ECD).

identity of these compounds remains unknown.

Typical FID Chromatograms are shown in Figures 57 and 58. A comparison of Chromatogram #3 and #7 in Figure 57 shows that ozonation of clearwell effluent water in PS 2 generally reduces the number of peaks. In Figure 57, 10 ft. of ozone-BAC tower (Chromatogram #C8-4) also reduces the number of peaks, as does the nonozone-BAC tower (Figure 58). In Figure 58, rechlorination of BAC tower effluents, Chromatograms #C-9 and #D-9, does not increase the number of FID peaks beyond the $C_6$ standard.

We conclude that ozonation reduces the number of FID peaks found in lime-softened water over the full capillary chromatogram. Rechlorination of BAC tower effluents does not increase the number of FID peaks beyond the $C_6$ standard.

## RESULTS FOR BACTERIOLOGICAL PARAMETERS STUDIED

### Results for Phase 2 of Pilot Plant Ozone-BAC Study

The mean, standard deviation, and range of the total plate counts/mL (TPC) obtained from each sample point on each of 26 sample dates during the experimental period are given in Table 35. Figure 59 is a graphic display of TPC/mL for each sample. Table 36 lists the frequency with which each kind of bacteria was recovered from each sample site. Table 37 shows the dominant bacteria listed in order of frequency of their dominance. Dominance was defined as greater than half of the TPC. Where two or more occurred in equal numbers, all were listed as dominant.

The TPC of the raw water (sample 1) ranged from 28 to 820 colonies/mL with a mean of 280 (Table 35). Lime-softening usually decreased the count. Counts were increased at sample point #3, the surge tank supplying influent to the MOC. Samples from point #7, ozone bubble contactor effluent, gave counts that were 100-fold less than those of the ozonator influent.

The mean of the bacterial count/mL obtained from the top of the GAC/$O_3$ tower effluent (C 8-1) was twice that from the top of the GAC/$O_2$ tower effluent (D 8-1), but the range of values was almost the same (Table 35). The same was true of the top sample (C 8-1) and bottom sample (C 8-4) of effluent from the GAC/$O_3$ tower. The bottom sample of effluent from the GAC/$O_2$ tower (D 8-4) had the greatest mean bacterial count/mL and its greatest count was four times the greatest count of the GAC/$O_3$ tower's top effluent. As all of the mean bacterial counts were variable with standard deviations much greater than the means, it is doubtful that this signifies that more favorable culture conditions existed in the lower part of the GAC/$O_2$ tower. Figure 59 Part C shows that on 11 out of the 26 sample dates, the counts/mL of the D 8-4 sample were greater than those from D 8-1, but the infrequent enormous count (e.g. $4.1 \times 10^7$ on 07/01/81) influenced the mean.

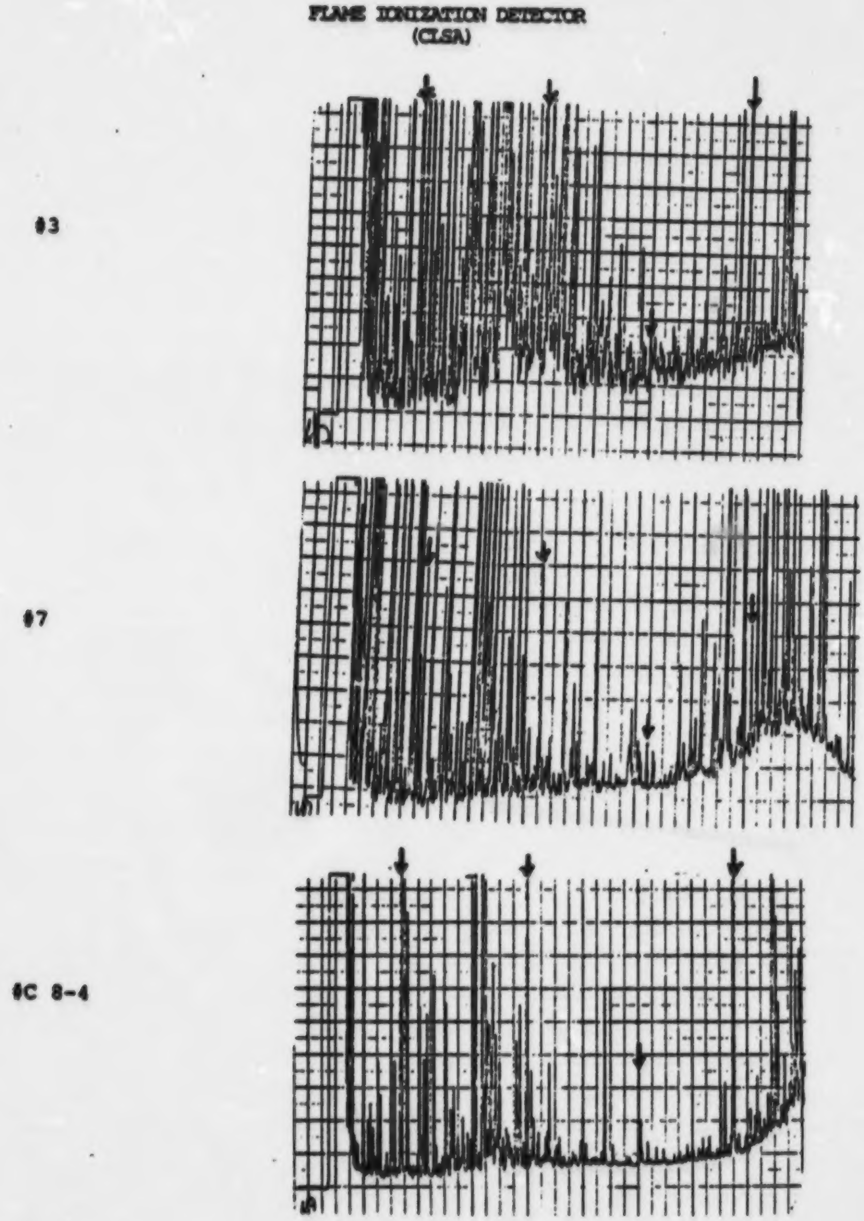
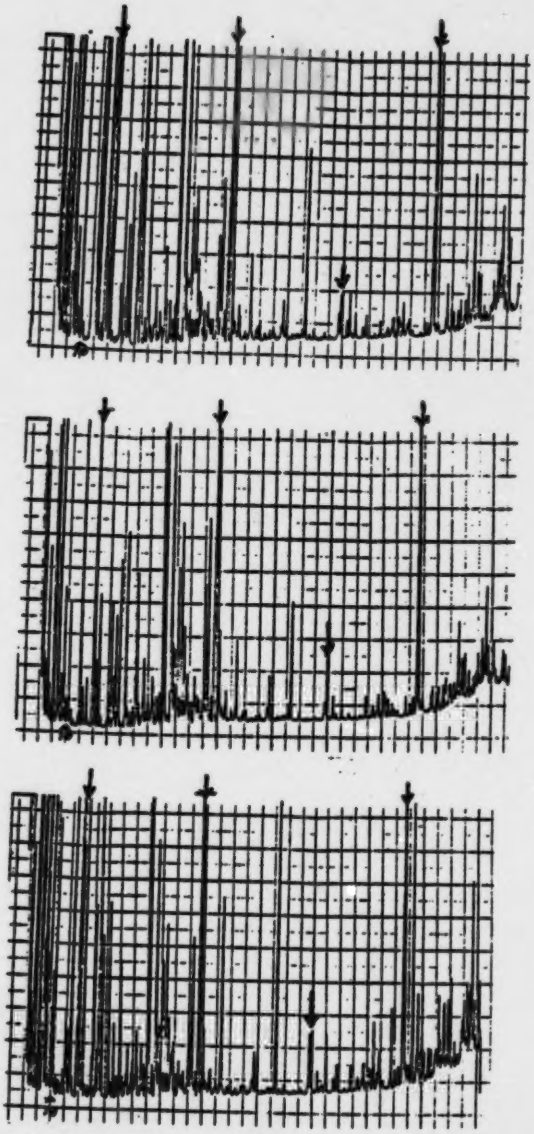


Figure 57. Closed-loop stripping analysis (capillary column-FID detector).

FLAME IONIZATION DETECTOR
(CLSA)



#C-9

#D 8-4

#D-9

Figure 58. Closed-loop stripping analysis (capillary column-FID detector).

## TABLE 35

## MEAN, STANDARD DEVIATION, AND RANGE OF TOTAL PLATE COUNT/mL OBTAINED FROM SAMPLES OF RAW, TREATED WATER, AND CARBON, PS 2, PHASE 1

| Sample | $\bar{x}$ | s.d. | Range |
|---|---|---|---|
| | | Supply Water | |
| 1 | 280 | 250 | 28-820 |
| 2 | 89 | 150 | 0->3,000 |
| 2P | 18 | 21 | 0-85 |
| 3 | 230,000 | 1,000,000 | 0-5,300,000 |
| 7 | 2,300 | 2,800 | 43-10,000 |
| | | Effluent and Carbon | |
| C 8-1 (effluent) | 1,200,000 | 2,700,000 | 0-10,000,000 |
| C-Top (carbon) | 390,000,000 | 1,300,000,000 | 0-6,100,000,000 |
| C 8-4 (effluent) | 570,000 | 1,700,000 | 0-8,200,000 |
| C-Bottom (carbon) | 420,000,000 | 1,700,000,000 | 0-7,700,000,000 |
| D 8-1 (effluent) | 590,000 | 2,000,000 | 0-9,600,000 |
| D-Top (carbon) | 240,000,000 | 890,000,000 | 0-4,100,000,000 |
| D 8-4 (effluent) | 1,700,000 | 8,000,000 | 0-41,000,000 |
| D-Bottom (carbon) | 180,000,000 | 540,000,000 | 0-2,400,000,000 |
| | | Tower Effluent, Chlorinated and Aged | |
| C-9 | 1,900 | 5,600 | 0-25,000 |
| C-9+2 | 3,400 | 13,000 | 0-57,000 |
| C-9+6 | 100,000 | 170,000 | 0-510,000 |
| D-9 | 440 | 990 | 0-3,500 |
| D-9+2 | 85,000 | 300,000 | 0-1,400,000 |
| D-9+6 | 44,000 | 140,000 | 0-560,000 |

## TABLE 36

## FREQUENCY OF OCCURRENCE OF BACTERIA DURING PS 2, PHASE 1

Sample Site

| Organism | 1 | 2 | 2P | 3 | 7 |
|---|---|---|---|---|---|
| None | 0 | 4 | 8 | 4 | 0 |
| Unidentified* | 35 | 69 | 85 | 46 | 46 |
| Alcaligenes spp. | 7 | 8 | - | 12 | 23 |
| A. lwoffi | 23 | 15 | - | 19 | 19 |
| Moraxella spp. | 54 | 23 | 8 | 35 | 38 |
| Pseudomonas spp. | 12 | 4 | - | 8 | 15 |
| pseudomonads | 27 | 15 | 4 | 42 | 27 |
| CDC Group | - | - | - | - | 4 |
| Flavobacterium | 4 | - | - | - | - |
| Yeast | 4 | - | - | 4 | 4 |
| G + rod | 28 | 28 | - | 4 | 4 |
| G + cocci | 12 | 14 | 8 | 15 | 12 |

## TABLE 36 (continued)

## FREQUENCY OF OCCURRENCE OF BACTERIA DURING PS 2, PHASE 1

Sample Site

| Organism | C8-1 | CTOP | D8-1 | DTOP | C8-4 | CBOT | D8-4 | DBOT |
|---|---|---|---|---|---|---|---|---|
| None | 4 | 12 | 4 | 12 | 4 | 12 | 8 | 19 |
| Unidentified* | 62 | 50 | 73 | 65 | 58 | 73 | 54 | 62 |
| Alcaligenes spp. | 12 | 8 | 8 | 8 | 19 | 4 | 12 | 8 |
| A. lwoffi | 23 | 12 | 15 | 4 | 19 | - | 19 | - |
| Moraxella spp. | 27 | 27 | 12 | - | 19 | 4 | 31 | 12 |
| Pseudomonas spp. | 12 | 4 | - | 8 | 4 | 8 | - | 8 |
| pseudomonads | 4 | 8 | 8 | 4 | 27 | 4 | 19 | 4 |
| CDC Group | - | - | - | - | - | - | - | - |
| Flavobacterium | - | - | - | - | - | - | - | - |
| Yeast | 4 | - | - | - | 4 | - | 4 | 28 |
| G + rod | - | 4 | 4 | - | - | - | 4 | - |
| G + cocci | 8 | 8 | 8 | 4 | 4 | - | 12 | - |

## TABLE 36 (continued)

## FREQUENCY OF OCCURRENCE OF BACTERIA DURING PS 2, PHASE 1

| | Sample Site | | | | | | |
|---|---|---|---|---|---|---|---|
| Organism | C-9 | C-9+2 | C-9+6 | D-9 | D-9 | D-9+2 | D-9+6 |
| None | 35 | 17 | 19 | 42 | 42 | 50 | 42 |
| Unidentified* | 42 | 42 | 69 | 46 | 46 | 42 | 46 |
| Alcaligenes spp. | 4 | 8 | 8 | - | - | - | 4 |
| A. lwoffi | 4 | - | - | 4 | 4 | - | 4 |
| Moraxella spp. | 8 | - | - | 12 | 12 | - | - |
| Pseudomonas spp. | 4 | 8 | - | - | - | - | 4 |
| pseudomonads | 4 | - | 4 | 8 | 8 | - | 12 |
| CDC Group | - | - | - | - | - | - | - |
| Flavobacterium | - | 4 | - | - | - | - | - |
| Yeast | - | - | - | - | - | - | - |
| G + rod | 4 | - | 4 | 4 | 4 | 4 | - |
| G + cocci | - | - | 4 | 4 | 4 | - | - |

*Unidentified species include unidentifiable bacteria and those not attempted because the TPC was outside the range of the dilution used.

## TABLE 37

## BACTERIA DOMINANT IN TPC DURING PS 2, PHASE 1, IN ORDER OF DOMINANCE FREQUENCY

(parentheses: equal frequency)

| Sample Site | Dominant Bacteria in Order of Frequency |
|---|---|
| 1 | Unidentified spp, Moraxella spp., Acinetobacter spp., Alcaligenes spp., (Pseudomonas spp., G + cocci) |
| 2 | Unidentified spp., Moraxella spp., (Alcaligenes spp. Acinetobacter spp., pseudomonads, G + rods) |
| 2P | Unidentified spp., (Alcaligenes spp., Acinetobacter spp., G + cocci, Moraxella spp.) |
| 3 | Unidentifed spp., Moraxella spp., Acinetobacter spp., pseudomonads, (Alcaligenes spp., G + cocci) |
| 7 | Unidentified spp., (Moraxella spp., Acinetobacter spp.), (Alcaligenes spp., G + cocci, pseudomonads), (Pseudomonas spp., CDC Groups, Flavobacterium spp.) |
| C 8-1 | Unidentified spp., Acinetobacter spp., (G + cocci, Moraxella spp.), yeast |
| C Top | Unidentified spp., Moraxella spp., (Acinetobacter spp. G + cocci), (G + rods, Pseudomonas spp.) |
| D 8-1 | Unidentified spp., Acinetobacter spp., G + cocci, (Moraxella spp., pseudomonads) |
| D Top | Unidentified spp., (Alcaligenes spp., Pseudomonas spp.), Moraxella spp. |
| C 8-4 | Unidentified spp., Acinetobacter spp., Moraxella spp., (Alcaligenes spp., G + rods, yeast, pseudomonads) |
| C Bot | Unidentified spp., Pseudomonas spp., (Alcaligenes spp., Moraxella spp.) |
| D 8-4 | Unidentified spp., Acinetobacter spp., (Alcaligenes spp., Moraxella spp.), (G + cocci, yeast) |
| D Bot | Unidentified spp., Moraxella spp., (Alcaligenes spp., yeast, pseudomanas spp.) |
| C-9 | Unidentified spp., (Acinetobacter spp., Alcaligenes spp., G + rods, Moraxella spp., Pseudomonas spp.) |

TABLE 37 (continued)

| Sample Site | Dominant Bacteria in Order of Frequency, |
|---|---|
| C-9+2 | Unidentified spp. (*Alcaligenes* spp., *Pseudomonas* spp., *Flavobacterium* spp.) |
| C-9+6 | Unidentified spp., *Alcaligenes* spp., G + rods |
| D-9 | Unidentified spp., *Moraxella* spp., (G + cocci, G + rods, pseudomonads) |
| D-9+2 | Unidentified spp., (G + cocci, G + rods) |
| D-9+6 | Unidentified spp., (*Alcaligenes* spp., *Pseudomonas* spp., pseudomonads) |

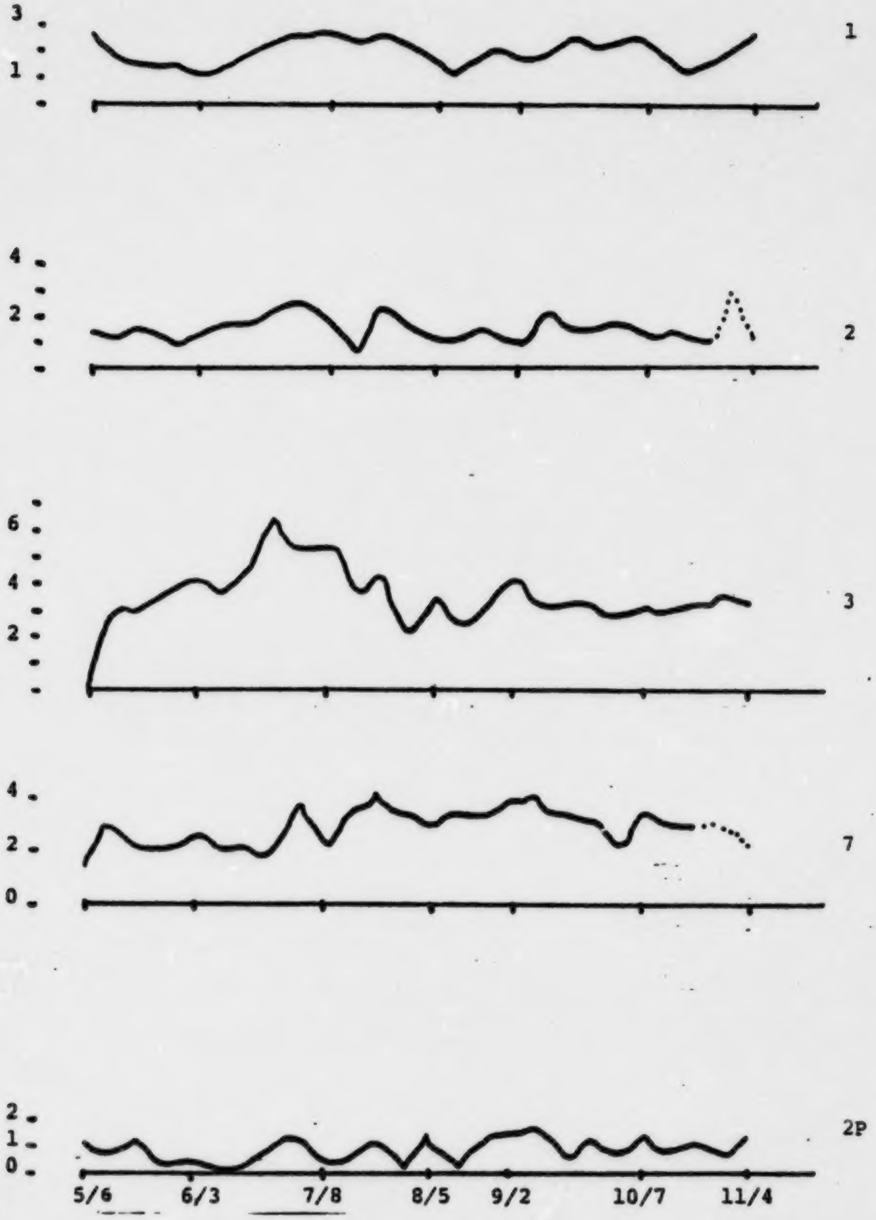


Figure 59a. Total plate counts/mL, $\log_{10}$. Dotted line, dilution limit exceeded. Supply water samples 1 through 7, PS 2, phase 1.

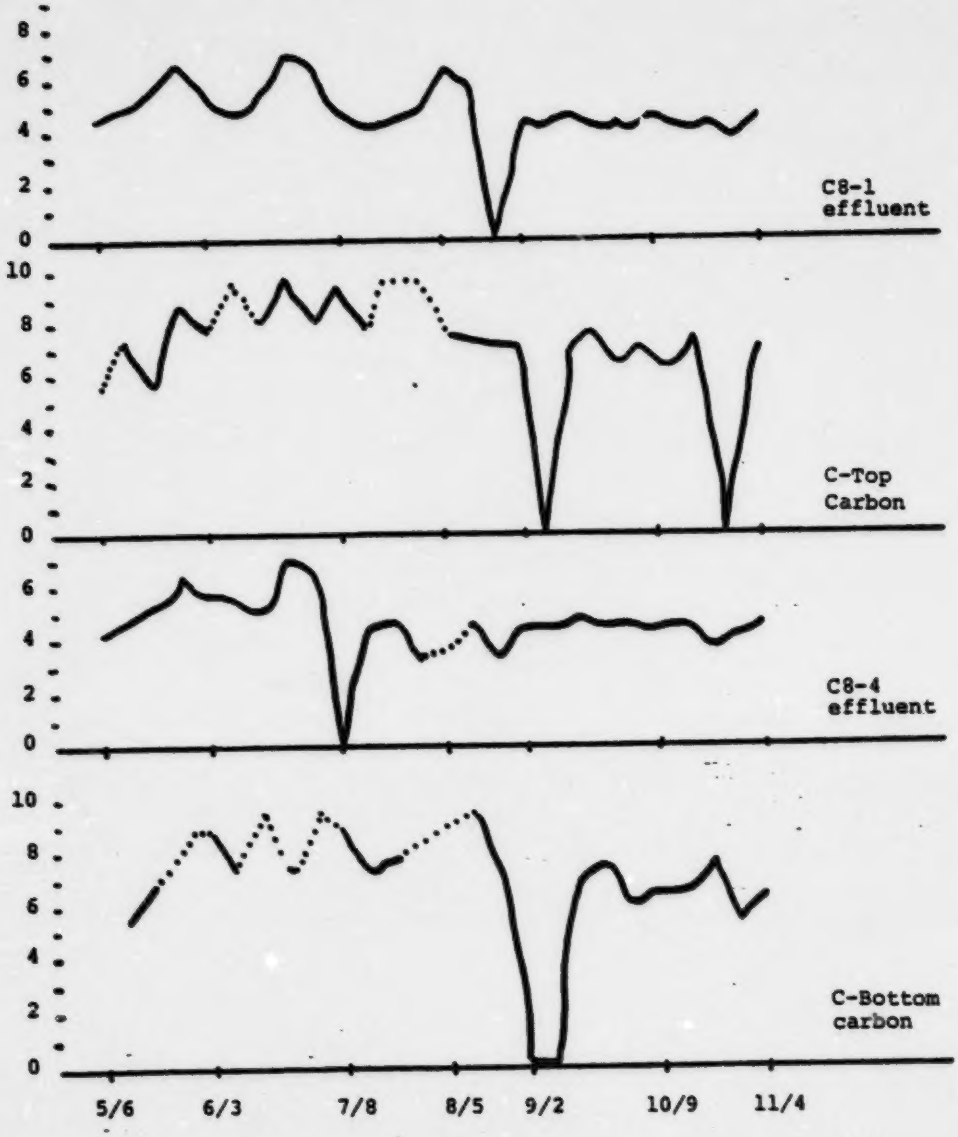


Figure 59b. Total plate counts/mL, $\log_{10}$. Dotted line, dilution limit exceeded. Aerated carbon tower effluent and carbon samples, during PS2, phase 1.

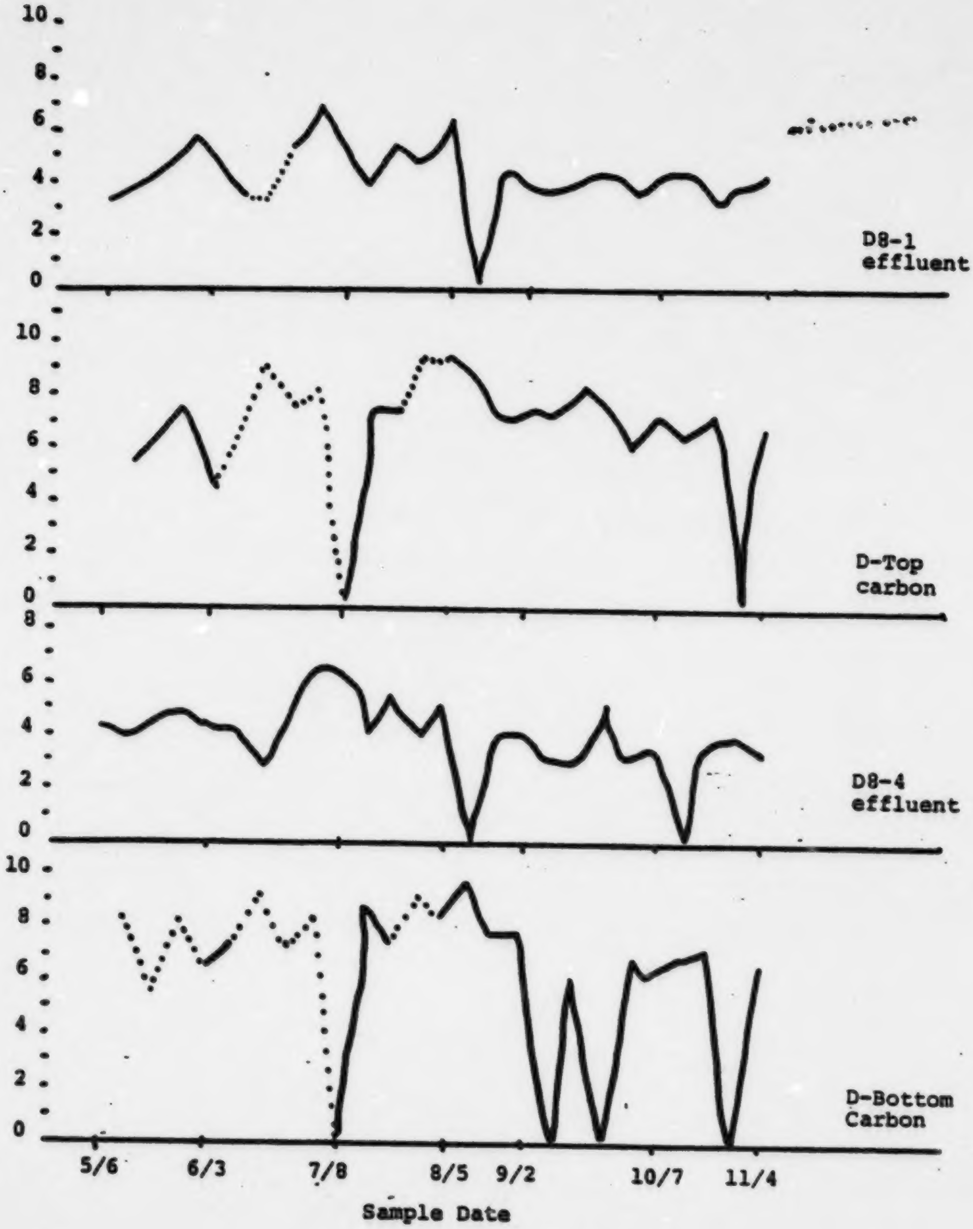


Figure 59c. Total plate counts/mL, $\log_{10}$. Dotted line, dilution limit exceeded. Ozonated carbon tower effluent and carbon samples, during PS2, phase 1.

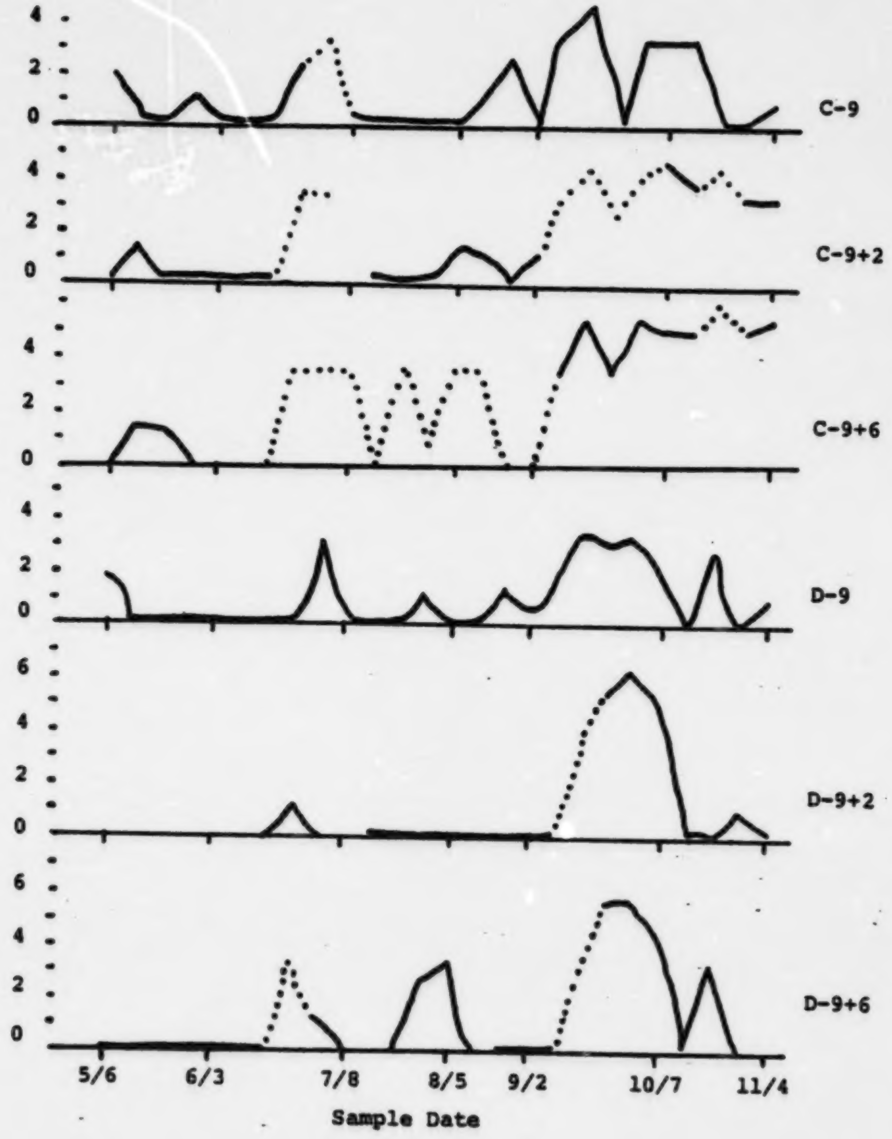


Figure 59d. Total plate counts/mL, $\log_{10}$. Dotted line, dilution limit exceeded. Effluents, chlorinated and aged samples, during PS2, phase 1.

Counts/mL obtained from carbon samples taken from the upper and lower sample ports of both GAC towers were much greater than previously reported, and ranged from hundreds of millions/mL up to several billions/mL (Table 35).

In comparing the counts of the two carbon tower effluents and carbon, the GAC/$O_2$ bottom effluent had greater mean counts; the GAC/$O_3$ top effluent had greater mean counts than their opposites. Carbon in the top of both towers gave the same mean counts and the bottom samples of carbon from the GAC/$O_3$ tower had counts twice as great as that from the GAC/$0_2$ tower. The ranges of counts agree with the means except that the ranges of C 8-1 and D 8-1 effluents, top) are the same, whereas the means differ by a factor of two, the GAC/$O_3$ being greater.

No comparison can be made from top to bottom of each carbon tower as the counts were more often different (16 times out of 26, C top and bottom; and 14 times out of 26, D top and bottom) than similar and were not consistently higher in one or the other location.

Counts that exceeded the dilution factor (indicated by "greater than") were not uncommon and because of the variability in samples from one sample date to another, it was impossible to anticipate these counts. These observations emphasize the dynamic nature of the bacterial system in the carbon bed.

Many unidentified bacteria that did not survive subculture and those that did not fit taxonomic keys were observed. These probably have little public health significance, but as they often occurred in large numbers and were the most frequently dominant kind found, may contribute significantly to the metabolic activity in the carbon bed. Other bacteria found were common aquatic forms.

Bacteria that were recovered from chlorinated samples were of all the kinds represented and probably survived inside sloughed-off cell aggregates that protected them from disinfectant.

The bacteria isolated from these samples were common water and soil organisms and the same as those found in all phases of this work.

The counts/mL recovered from all GAC effluents generally were ten times greater than in PS 1. The TPC recovered from carbon samples greatly exceeded any previously reported and probably reflect improved sonication technique rather than a quantitative difference in the populations that developed in the carbon beds.

Little or no difference was found in numbers or kinds of bacteria recovered from samples of water treated by ozone or air after 2 days of holding samples.

Differences in means of counts, as a basis for comparison of effects of ozonation and aeration on bacteria, were inadequate because of overlapping variability of these values around their means.

## Bacterial Profile on Separate Experiment to Measure Double-Bond Compound Removal by Ozone

Bacterial total plate counts obtained during this phase of the work are given in Tables 38, 39, and 40.

The number of all bacteria recovered from samples after ozone treatment, although reduced (mean = 570/mL) from that of the influent (mean = 2600/mL), indicated that the level of ozone applied was not adequate for disinfection.

The TPC obtained from 1-hour samples following either ozonation and aeration were not different from respective samples analyzed immediately after either treatment. During the 6-day holding time, the aerated samples apparently developed greatest TPC in 2 days, which decreased after 6 days, and the TPC of the ozonated samples reached the maximum after 6 days. These apparent differences should be considered in view of the variability of individual sample values, keeping in mind the slight differences in the influent samples (#3) in each part of the experiment, which developed population sizes in the same way.

The numbers of bacteria recovered from influent samples (#3 series) were relatively high for well water from this site and ranged from 260 to greater than 3000/mL (Tables 38 and 39). In previous experiments, influent samples yielded counts of 100/mL or less. The air- and ozone-treated samples had similar bacteria counts; air, $\bar{x}$ = 2500/mL and ozone, $\bar{x}$ = 2600/mL. The nonchlorinated aerated influent sample reached a peak population size in two days and decreased in six days; the ozone influent sample increased to reach its greatest size in six days. This difference, however, is lost in the variability of the means: C.V. = 80% for air influent samples and 180% for the ozone influent samples.

Chlorinated aerated samples developed bacteria after 6 days; chlorinated ozonated samples did not. Samples of chlorinated influent also developed bacteria after low (1 - 4/mL), 1-hour aged counts were recorded.

Instantaneous influent counts of 260 to greater than 3000/mL were reduced by chlorine to 1 or less except in 3 samples: influent samples 3 and 4 during ozonation and influent sample 7 during aeration. In these, counts of greater than 3000/mL were obtained as was obtained from the unchlorinated instantaneous influent sample. Influent counts greater than 3000/mL were not expected, as raw water from Preston plant wells usually yields counts of less than 100/mL, and thus dilutions for the pour plate method chosen to accommodate the lower counts were inadequate for enumerating the bacteria recovered from these samples. No adjustment could be made during the course of the experiment because the duration of the experiment was shorter than incubation time required to reveal the greater population found in these samples.

# TABLE 38

## PS 2, PHASE 2 OZONE APPLICATION, TOTAL PLATE COUNT/mL

| | | SAMPLE AGE | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | #3 | | | | #7 | | | |
| Sample | | Inst. | 1 Hour | 2 Days | 6 Days | Inst. | 1 Hour | 2 Days | 6 Days |
| 1 | NoCl$_2$ | >3,000 | >3,000 | 71,000 | 15,000 | 420 | *140 | 230,000 | 360,000 |
| | Cl$_2$ | | 4 | 0 | 0 | | *1 | 0 | 0 |
| 2 | NoCl$_2$ | >3,000 | >3,000 | 63,000 | 23,000 | 300 | 300 | 300,000 | 100,000 |
| | Cl$_2$ | | 0 | 0 | 0 | | 0 | 0 | 0 |
| 3 | NoCl$_2$ | >3,000 | >3,000 | 57,000 | 5,000 | 400 | 420 | 210,000 | 4,000,000 |
| | Cl$_2$ | | >3,000 | 0 | 0 | | 0 | 0 | 0 |
| 4 | NoCl$_2$ | >3,000 | >3,000 | 46,000 | 15,000 | 300 | >3,000 | 170,000 | 150,000 |
| | Cl$_2$ | | >3,000 | 0 | 0 | | 340 | 0 | 0 |
| 5 | NoCl$_2$ | 2,400 | 3,400 | 70,000 | 2,400,000 | 490 | 590 | 410,000 | 53,000 |
| | Cl$_2$ | | 1 | 0 | 0 | | 4 | 0 | 0 |
| 6 | NoCl$_2$ | 4,500 | 3,100 | 130,000 | 150,000 | 600 | 480 | 210,000 | 68,000 |
| | Cl$_2$ | | 1 | 0 | 0 | | 4 | 0 | 0 |
| 7 | NoCl$_2$ | 260 | 2,400 | 320,000 | 100,000 | 1,700 | 700 | 240,000 | 360,000 |
| | Cl$_2$ | | 0 | 0 | 0 | | 0 | 0 | 0 |
| 8 | NoCl$_2$ | 3,100 | 4,200 | 400,000 | 4,100,000 | 350 | 3,900 | 370,000 | 1,400,000 |
| | Cl$_2$ | | 0 | 0 | 22,000 | | 0 | 0 | 0 |

*Fungi - probable air contaminant

## TABLE 39

## PS 2, PHASE 2 AIR APPLICATION, TOTAL PLATE COUNT/mL

| | | SAMPLE AGE | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | #3 | | | | #7 | | | |
| Sample | | Inst. | 1 Hour | 2 Days | 6 Days | Inst. | 1 Hour | 2 Days | 6 Days |
| 1 | $NoCl_2$ | 1,700 | 970 | 30,000 | 69,000 | 730 | 750 | 9,000 | 120,000 |
| | $Cl_2$ | | 2 | 0 | 0 | | 7 | 0 | 0 |
| 2 | $NoCl_2$ | 690 | 730 | 400,000 | 96,000 | 560 | 790 | >30,000 | 140,000 |
| | $Cl_2$ | | 0 | 0 | 0 | | 2 | 0 | 0 |
| 3 | $NoCl_2$ | 430 | 570 | 56,000 | 94,000 | 370 | 710 | 500,000 | 76,000 |
| | $Cl_2$ | | 0 | 0 | 0 | | 11 | 0 | 0 |
| 4 | $NoCl_2$ | 700 | 1,400 | 250,000 | 81,000 | 640 | 620 | 600,000 | 99,000 |
| | $Cl_2$ | | 0 | 0 | 0 | | 0 | 0 | 0 |
| 5 | $NoCl_2$ | 5,400 | 4,800 | 610,000 | 270,000 | 7,800 | 4,800 | 29,000 | 160,000 |
| | $Cl_2$ | | 0 | 0 | 0 | | 0 | 0 | 200 |
| 6 | $NoCl_2$ | 4,800 | 1,600 | 90,000 | 190,000 | 6,000 | 4,200 | 510,000 | 600,000 |
| | $Cl_2$ | | 0 | 0 | 0 | | 0 | 0 | 100 |
| 7 | $NoCl_2$ | 3,600 | >3,000 | 90,000 | 500,000 | 7,800 | >3,000 | 540,000 | 120,000 |
| | $Cl_2$ | | >3,000 | 0 | >3,000 | | 0 | 0 | 0 |
| 8 | $NoCl_2$ | >3,000 | 2,300 | 450,000 | 150,000 | >3,000 | 5,400 | 410,000 | 420,000 |
| | $Cl_2$ | | 0 | 100 | 100 | | 0 | 0 | 0 |

# TABLE 40

## TOTAL PLATE COUNTS/mL
## COMPARISON OF MEANS & VARIABILITY OF CHLORINATED AND NON-CHLORINATED WATER TREATED WITH OZONE AND AIR

SAMPLE AGE

| Sample | #3 | | | | #7 | | | |
|---|---|---|---|---|---|---|---|---|
| | Inst. | 1 Hour | 2 Days | 6 Days | Inst. | 1 Hour | 2 Days | 6 Days |
| Air, No$Cl_2$ | | | | | | | | |
| N | 7 | 7 | 8 | 8 | 7 | 7 | 7 | 8 |
| x | 2,500 | 1,800 | 250,000 | 180,000 | 3,400 | 2,500 | 370,000 | 220,000 |
| S.D. | 2,100 | 1,500 | 220,000 | 150,000 | 3,600 | 2,200 | 250,000 | 190,000 |
| C.V.,% | 85 | 83 | 88 | 80 | 100 | 90 | 67 | 87 |
| Air, $Cl_2$ | | | | | | | | |
| N | 7 | 7 | 8 | 7 | 7 | 8 | 8 | 8 |
| x | 2,500 | <1 | 13 | 14 | 3,400 | 3 | 0 | 38 |
| S.D. | 2,100 | 0.8 | 35 | 38 | 3,600 | 4 | 0 | 74 |
| C.V.,% | 85 | 270 | 270 | 270 | 100 | 130 | 0 | 190 |
| 03, No$Cl_2$ | | | | | | | | |
| N | 4 | 4 | 8 | 8 | 8 | 7 | 8 | 8 |
| x | 2,600 | 3,300 | 140,000 | 850,000 | 570 | 930 | 270,000 | 820,000 |
| S.D. | 1,800 | 750 | 140,000 | 1,500,000 | 470 | 1,300 | 84,000 | 1,400,000 |
| C.V.,% | 69 | 23 | 94 | 180 | 82 | 140 | 32 | 180 |
| 03, $Cl_2$ | | | | | | | | |
| N | 4 | 6 | 8 | 8 | 8 | 8 | 8 | 8 |
| x | 2,600 | 1 | 0 | 2,700 | 570 | 44 | 0 | 0 |
| S.D. | 1,800 | 2 | 0 | 7,600 | 470 | 120 | 0 | 0 |
| C.V.,% | 69 | 200 | 0 | 280 | 82 | 270 | 0 | 0 |

Only in two samples, influent sample #4 (3A4) during aeration and effluent sample #4 (7A4) during aeration, was free chlorine detected after 2 days of aging (Table 41). Sample 3A4 had 0.29 ppm and sample 7A4 had 0.03 ppm residual free chlorine after 2 days of aging. Neither of these samples developed detectable bacteria (Table 39). Bacteria grew in samples 3A7, 3A8, 7A5, 7A6, and 3-8, where no residual free chlorine was detected after two days (Tables 38 and 39).

Neither coliforms nor *Pseudomonas aeruginosa* was found in any of the samples taken during the 4-day experimental period.

Table 42 lists kinds and numbers of bacteria recovered from each sample that yielded bacteria during this experiment. The frequency of occurrence of each kind in the eight samples taken from each sample point is given in Table 42.

*Alcaligenes* spp., *Moraxella* spp., and *Pseudomonas stutzeri* were found in ozonated water samples that were not chlorinated, when these samples were plated instantaneously or after holding for 1 hr after ozonation. Unidentified species (i.e., those that did not survive subculturing or defied the identification process) were recovered from instantaneously plated samples and were the only kind that grew from samples that were aged for 6 days, except for one sample, which yielded *Alcaligenes* spp.

*Alcaligenes* spp. were found in samples of ozonated water, but not in samples of aerated water. This may indicate that the composition of organic solutes produced by ozone treatment enhanced the development of *Alcaligenes* populations. *Alcaligenes* spp. may have been more ozone tolerant, or better protected by slime films than other bacteria that were present. Perhaps *Alcaligenes* spp. then grew more prolifically in the absence of more susceptible species, whereas they may have been suppressed in mixed cultures in non-ozonated water. On the other hand, *Alcaligenes* spp. were more prevalent in the influent during ozonation than during aeration and their appearance in ozonated effluent may simply reflect this. *Moraxella* similarly was common in ozonated effluent and not as common in aerated effluent. *Moraxella*, however, was equally common in the influent of both treatments.

All of the bacteria identified were normal inhabitants of organic-laden local waters. The unidentified bacteria were probably common soil and water species, as loss on subculture is routinely encountered when dealing with soil and water samples. Simulation of the conditions of their natural habitat is almost impossible, as it is a complex environment, probably dependent on micronutrient balances and biotic interactions that are not yet clearly understood.

The following observations were made during these experiments:

Chlorine was an effective disinfectant for 6 days in water samples that developed total plate counts of up to 4 million/mL in non-chlorinated comparison samples.

## TABLE 41

## BREAKPOINT CHLORINATION, CHLORINE RESIDUALS

| Sample No. | 1 Hour |  | 2 Days |  | 6 Days |  |
|---|---|---|---|---|---|---|
|  | Free | Comb. | Free | Comb.* | Free | Comb.* |
| 3-1 | 1.06 | 0.34 | 0.0 | 0.14 | 0.0 | 0.03 |
| 7-1 | 0.94 | 0.31 | 0.0 | 0.05 | 0.0 | 0.03 |
| 3-2 | 0.56 | 0.34 | 0.0 | 0.09 | 0.0 | 0.03 |
| 7-2 | 0.94 | 0.31 | 0.0 | 0.09 | 0.0 | 0.03 |
| 3-3 | 0.78 | 0.34 | 0.0 | 0.12 | 0.0 | 0.03 |
| 7-3 | 0.91 | 0.31 | 0.0 | 0.05 | 0.0 | 0.03 |
| 3-4 | 0.11 | 0.31 | 0.0 | 0.03 | 0.0 | 0.03 |
| 7-4 | 0.08 | 0.34 | 0.0 | 0.03 | 0.0 | 0.03 |
| 3-5 | 2.01 | 0.37 | 0.0 | 0.26 | 0.0 | 0.08 |
| 7-5 | 2.11 | 0.31 | 0.0 | 0.14 | 0.0 | 0.0 |
| 3-6 | 1.59 | 0.34 | 0.0 | 0.09 | 0.0 | 0.05 |
| 7-6 | 1.77 | 0.30 | 0.0 | 0.21 | 0.0 | 0.0 |
| 3-7 | 0.61 | 0.31 | 0.0 | 0.09 | 0.0 | 0.0 |
| 7-7 | 2.58 | 0.30 | 0.0 | 0.23 | 0.0 | 0.0 |
| 3-8 | 1.67 | 0.43 | 0.0 | 0.12 | 0.0 | 0.0 |
| 7-8 | 0.08 | 1.36 | 0.0 | 1.24 | 0.0 | 0.16 |
| 3A-1 | 2.26 | 0.39 | 0.0 | 0.26 | 0.0 | 0.12 |
| 7A-1 | 1.27 | 0.35 | 0.0 | 0.05 | 0.0 | 0.06 |
| 3A-2 | 0.97 | 0.32 | 0.0 | 0.05 | 0.0 | 0.03 |
| 7A-2 | 0.06 | 0.88 | 0.0 | 0.05 | 0.0 | 0.0 |
| 3A-3 | 0.09 | 0.80 | 0.0 | 0.34 | 0.0 | 0.03 |
| 7A-3 | 0.05 | 1.50 | 0.0 | 0.69 | 0.0 | 0.27 |
| 3A-4 | 3.09 | 0.44 | 0.29 | 0.43 | 0.0 | 0.12 |
| 7A-4 | 3.27 | 0.44 | 0.03 | 0.38 | 0.0 | 0.15 |
| 3A-5 | 1.67 | 0.39 | 0.0 | 0.13 | 0.0 | 0.04 |
| 7A-5 | 1.16 | 0.35 | 0.0 | 0.08 | 0.0 | 0.03 |
| 3A-6 | 2.28 | 0.39 | 0.0 | 0.17 | 0.0 | 0.12 |
| 7A-6 | 1.42 | 0.39 | 0.0 | 0.08 | 0.0 | 0.03 |
| 3A-7 | 2.51 | 0.35 | 0.0 | 0.30 | 0.0 | 0.18 |
| 7A-7 | 1.84 | 0.44 | 0.0 | 0.17 | 0.0 | 0.10 |
| 3A-8 | 2.09 | 0.40 | 0.0 | 0.20 | 0.0 | 0.0 |
| 7A-8 | 1.98 | 0.39 | 0.0 | 0.17 | 0.0 | 0.07 |

Combined chlorine residual of <0.05 should be considered zero.

## TABLE 42

## BACTERIA SPECIES ISOLATED FROM OZONE AND AIR TREATED WATER SAMPLES DURING PS 2, PHASE 2 LISTED BY SPECIES, COLONIES/mL

| Influent | | | | Effluent | | | |
|---|---|---|---|---|---|---|---|
| Sample | Sample Age | Air | 0 | Sample | Sample Age | Air | 0 |
| Unidentified | | | | | | | |
| 3-1 | inst. | 580 | >3,000 | 7-1 | inst. | 730 | 420 |
| 3-2 | inst. | 690 | >3,000 | 7-2 | inst. | 560 | 20 |
| 3-2 | inst. | 690 | >3,000 | 7-3 | inst. | 370 | 150 |
| 3-3 | inst. | 430 | >3,000 | 7-4 | inst. | 640 | |
| 3-4 | inst. | | >3,000 | 7-5 | inst. | 7,800 | |
| 3-5 | inst. | 5,400 | 390 | 7-6 | inst. | 6,000 | 420 |
| 3-6 | inst. | 4,800 | 4,500 | 7-7 | inst. | 7,800 | 1,700 |
| 3-7 | inst. | 3,600 | 260 | 7-8 | inst. | 3,000 | |
| 3-8 | inst. | | 3,100 | 7-1 | 1 hour | 750 | 140 |
| 3-1 | 1 hour | 970 | >3,000 | 7-1 Cl | 1 hour | 7 | 1 |
| 3-1 Cl | 1 hour | 2 | 4 | 7-2 | 1 hour | 790 | 140 |
| 3-2 | 1 hour | 730 | >3,000 | 7-3 | 1 hour | 710 | |
| 3-3 | 1 hour | 570 | >3,000 | 7-3 Cl | 1 hour | 11 | |
| 3-3 Cl | 1 hour | | >3,000 | 7-4 | 1 hour | 620 | >3,000 |
| 3-4 | 1 hour | | >3,000 | 7-5 | 1 hour | 4,800 | |
| 3-4 Cl | 1 hour | | >3,000 | 7-5 Cl | 1 hour | | 4 |
| 3-5 | 1 hour | 4,800 | 3,400 | 7-6 | 1 hour | 4,200 | 330 |
| 3-5 Cl | 1 hour | | 1 | 7-6 Cl | 1 hour | | 4 |
| 3-6 | 1 hour | 800 | 3,100 | 7-7 | 1 hour | 3,000 | |
| 3-6 Cl | 1 hour | | 1 | 7-7 Cl | 1 hour | 3,000 | |
| 3-7 | 1 hour | >3,000 | 480 | 7-8 | 1 hour | 5,400 | 3,900 |
| 3-7 Cl | 1 hour | >3,000 | | 7-20 | 1 hour | 2 | |
| 3-8 | 1 hour | | 4,200 | 7-1 | 2 days | | 230,000 |
| 3-1 | 2 days | 30,000 | 71,000 | 7-2 | 2 days | >30,000 | |
| 3-2 | 2 days | 400,000 | 63,000 | 7-3 | 2 days | 500,000 | |
| 3-3 | 2 days | | 57,000 | 7-4 | 2 days | 600,000 | |
| 3-4 | 2 days | 250,000 | 46,000 | 7-5 | 2 days | 29,000 | 410,000 |
| 3-5 | 2 days | 610,000 | | 7-6 | 2 days | 510,000 | 210,000 |
| 3-6 | 2 days | | 46,000 | 7-7 | 2 days | 540,000 | 240,000 |
| 3-7 | 2 days | | 320,000 | 7-8 | 2 days | 410,000 | 370,000 |
| 3-8 | 2 days | 450,000 | 400,000 | 7-1 | 6 days | 120,000 | 360,000 |
| 3-8 Cl | 2 days | 100 | | 7-2 | 6 days | 140,000 | 100,000 |
| 3-1 | 6 days | 17,000 | 15,000 | 7-3 | 6 days | 76,000 | 4,000,000 |
| 3-2 | 6 days | 19,000 | 23,000 | 7-4 | 6 days | 370,000 | 150,000 |
| 3-3 | 6 days | 94,000 | 5,000 | 7-5 | 6 days | 53,000 | |
| 3-4 | 6 days | 81,000 | 15,000 | 7-5 Cl | 6 days | 200 | |
| 3-5 | 6 days | 270,000 | | 7-6 | 6 days | 600,000 | |
| 3-6 | 6 days | | 110,000 | 7-6 Cl | 6 days | 100 | |
| 3-7 | 6 days | 500,000 | | 7-7 | 6 days | 120,000 | |
| 3-7 Cl | 6 days | >3,000 | 22,000 | 7-8 | 6 days | 420,000 | |

## TABLE 42
## (CONTINUATION)

## BACTERIA SPECIES ISOLATED FROM OZONE AND AIR TREATED WATER SAMPLES DURING PS 2, PHASE 2 LISTED BY SPECIES, COLONIES/mL

| Influent |  |  |  | Effluent |  |  |  |
|---|---|---|---|---|---|---|---|
| Sample | Sample Age | Air | 0 | Sample | Sample Age | Air | 0 |
| **Moraxella Spp.** |  |  |  |  |  |  |  |
| 3-1 | inst. | 1,100 | 2,000 | 7-3 | inst. |  | 250 |
| 3-5 | inst. |  | 2,000 | 7-4 | inst. |  | 300 |
| 3-3 | 1 hour |  | 2,000 | 7-5 | inst. |  | 490 |
| 3-7 | 1 hour |  | 1,900 | 7-6 | inst. |  | 150 |
| 3-8 | 1 hour | 860 |  | 7-8 | inst. |  | 350 |
| 3-3 | 2 days | 56,000 |  | 7-3 | 1 hour |  | 390 |
| 3-6 | 2 days | 77,000 |  | 7-4 | 1 hour |  | 340 |
| 3-7 | 2 days | 90,000 |  | 7-5 | 1 hour |  | 590 |
|  |  |  |  | 7-6 | 1 hour |  | 150 |
|  |  |  |  | 7-7 | 1 hour |  | 700 |
|  |  |  |  | 7-4 | 6 days | 62,000 |  |
|  |  |  |  | 7-5 | 6 days | 81,000 |  |
| **Alcaligenes Spp.** |  |  |  |  |  |  |  |
| 3-5 | 2 days |  | 70,000 | 7-2 | inst. |  | 280 |
| 3-6 | 2 days |  | 86,000 | 7-2 | 1 hour |  | 160 |
| 3-8 Cl | 2 days |  | *22,000 | 7-2 | 1 hour |  | 30 |
| 3-5 | 6 days |  | 2,400,000 | 7-6 | 6 days |  | 68,000 |
| 3-6 | 6 days | 110,000 | 39,000 | 7-7 | 6 days |  | 360,000 |
| 3-7 | 6 days |  | 100,000 | 7-8 | 6 days |  | 1,400,000 |
| 3-8 | 6 days |  | 4,100,000 |  |  |  |  |
| **Acinetobacter lwoffi** |  |  |  |  |  |  |  |
| no Cl |  |  |  | no Cl |  |  |  |
| 3-1 2 | 6 days | 52,000 |  | 7-5 2 | 6 days | 77,000 |  |
| 3-2 | 6 days | 77,000 |  |  |  |  |  |
| **P. stutzeri** |  |  |  |  |  |  |  |
|  |  |  |  | no Cl |  |  |  |
|  |  |  |  | 7-2 2 | 2 days |  | 300,000 |
|  |  |  |  | 7-4 | 2 days |  | 170,000 |

* Only sample with chlorine.

## TABLE 42
## (CONTINUATION)

## BACTERIA SPECIES ISOLATED FROM OZONE AND AIR TREATED WATER SAMPLES DURING PS 2, PHASE 2 LISTED BY SPECIES, COLONIES/mL

| Influent | | | | Effluent | | | |
|---|---|---|---|---|---|---|---|
| Sample | Sample Age | Air | 0 | Sample | Sample Age | Air | 0 |
| P. putida | | | | | | | |
| | | | | 7-1 no C1 | 2 days | 9,000 | |
| pseudomonads | | | | | | | |
| no Cl<br>3-6 2 | 1 hour | 810 | | | | | |
| 3-8 | 1 hour | 1,400 | | | | | |
| 3-6 | 2 days | 13,000 | | | | | |
| G + Rods | | | | | | | |
| no Cl<br>3-4 2 | inst. | 700 | | | | | |
| G + Cocci | | | | | | | |
| no Cl<br>3-4 2 | 1 hour | 1,400 | | | | | |

Ozone alone reduced initial counts by at least one order of magnitude, but 3-4 mg/L did not disinfect the water.

Ozonation followed by chlorination to breakpoint was effective in preventing bacterial regrowth for 6 days, but so was chlorine alone.

# APPENDIX A

## EXPERIMENTAL DESIGN 1:
## BENCH-SCALE STUDIES OF GAC TYPES

## A1 Phase 1, Bench-Scale Study of Four GAC's on Finished Water

### A11 Chemical Parameters

### A111 Bench-Scale Unit Design

In previous research work, Ref. 1 through 6, it was established that on Miami water, GAC was the best adsorbent because of its ability to remove both precursor substances, as measured by TOC and THMFP, and volatile HOC. Therefore, the first study in this Pilot Plant Research Project was designed to determine the best commercial GAC available for the pilot plant when it was completed. Four commercially available carbons were selected for the study by our project officer, based on other research work carried out by the Environmental Protection Agency. The four selected were:

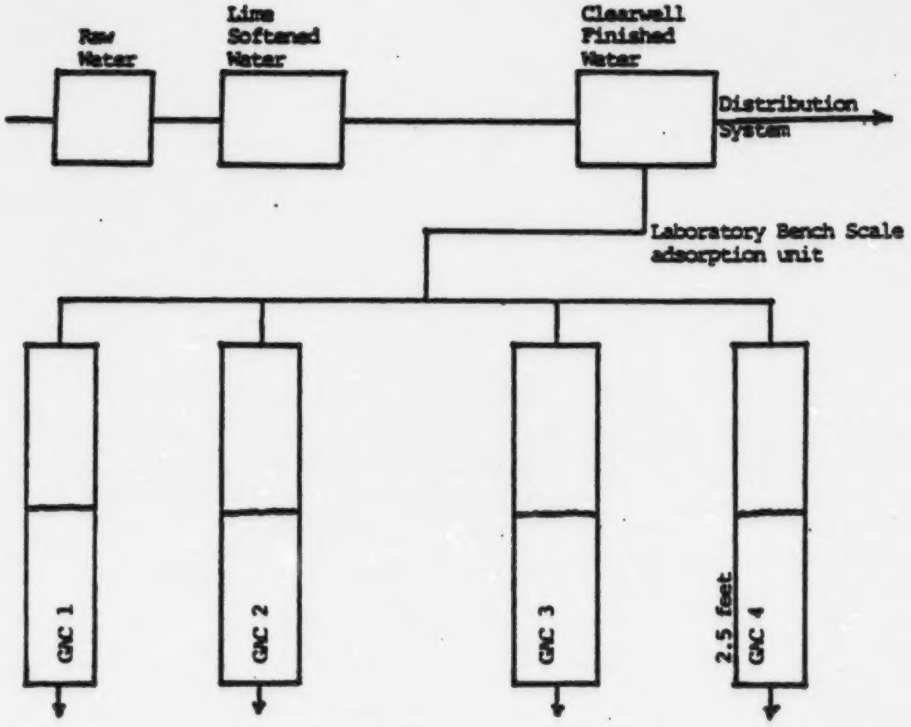
| | |
|---|---|
| Carbon 1 | Filtrasorb 400, 12 by 40 mesh, Calgon Corp, Pittsburg, Pennsylvania |
| Carbon 2 | Nuchar WVG, 12 by 40 mesh, Westvaco Corp., Covington, Virginia |
| Carbon 3 | Hydrodarco 1030, 10 by 30 mesh, ICI Americas, Inc., Wilmington, Delaware. |
| Carbon 4 | Witcarb Grade 950, 12 by 30 mesh, Witco Chemical Corp., New York, New York |

A bench-scale adsorption unit, (Figure 1) was set up in the laboratory at the Preston Water Treatment Plant.

Each glass adsorption column was one inch in diameter and 5 ft. tall, and contained an equal volume of carbon. The carbon bed depth was 2.5 ft. EBCT was 6.2 min. and each column received finished water from the clearwell at the Preston Plant. The influent and effluent concentration of TOC, THMFP and HOC was determined.

### A112 HOC Removal

The types of HOC and their average concentration (1975-1979) in µg/L in raw, lime-softened and finished water at the Preston Plant is shown in Table 1.



John E. Preston Water Treatment Plant

Hialeah, Florida

Raw Water
Lime Softened Water
Clearwell Finished Water
Distribution System
Laboratory Bench Scale adsorption unit
GAC 1
GAC 2
GAC 3
2.5 feet
GAC 4

Figure 1 Bench Scale Adsorption Unit Flow Diagram for the Study of Four Types of GAC on Finished Water

## TABLE 1

## AVERAGE CONCENTRATIONS OF PURGEABLE HALOGENATED ORGANIC COMPOUNDS IN RAW, LIME-SOFTENED AND FINISHED WATERS AT THE PRESTON PLANT HIALEAH, FLORIDA

| Compound | Average Concentration µg/L | | |
|---|---|---|---|
| | Raw Water | Lime Softened Water | Finished Water |
| Vinyl chloride | 12.8 | 9.7 | 6.2 |
| Methylene chloride | 0.45 | * | * |
| trans 1,2-dichloroethene | 1.5 | 0.95 | 0.77 |
| 1,1-Dichloroethane | 0.58 | 0.45 | 0.4 |
| cis 1,2-dichloroethene | 25.6 | 22.3 | 19.9 |
| Chloroform | 0.08 | 1.2 | 67.3 |
| 1,1,1-Trichloroethane | none | none | none |
| 1,2-Dichloroethane | 0.1 | 0.12 | 7.7 |
| Carbon tetrachloride | none | none | none |
| Trichloroethylene | 0.34 | 0.33 | 0.68 |
| Bromodichloromethane | † | 0.35 | 47 |
| Tetrachloroethylene | 0.003 | 0.004 | 0.003 |
| Chlorodibromomethane | † | 0.13 | 33.6 |
| Chlorobenzene | 1.1 | 0.72 | 0.86 |
| Bromoform | † | 0.007 | 2.6 |
| p-Chlorotoluene | 0.02 | 0.03 | 0.1 |
| m-Dichlorobenzene | † | † | † |
| p-Dichlorobenzene | 0.51 | 0.28 | 0.21 |
| o-Dichlorobenzene | 0.17 | 0.16 | 0.14 |
| TOTAL | 43.25 | 36.73 | 187.36 |

* Not determined

† Nil (present but below normal detection level)

As emphasis in this Pilot Plant research study was placed on removing THM precursor substances, only the effectiveness of the four GAC's to remove chloroform and TTHM will be discussed. Chloroform breakthrough curves are presented in Figure 2. These curves are typical of the relative performance of each GAC for all the HOC monitored. The results of integrating these breakthrough curves are shown in Table 2.

## TABLE 2

## PERCENTAGE OF CHLOROFORM REMOVAL BY FOUR TYPES OF GAC

| TYPE OF GAC | WEIGHT OF CARBON g | PERCENTAGE CHLOROFORM REMOVAL BY EQUAL VOLUME OF GAC | PERCENTAGE CHLOROFORM REMOVAL BY EQUAL WEIGHT OF GAC (172.4 g) |
|---|---|---|---|
| Carbon 1 | 163 | 53 | 56 |
| Carbon 2 | 195.6 | 40 | 36 |
| Carbon 3 | 144.1 | 48 | 58 |
| Carbon 4 | 172.4 | 78 | 78 |

On an equal volume basis, Carbon 4 exhibited the largest adsorptive capacity with 78 percent removal of chloroform, followed by Carbons 1, 3 and 2 with 53, 48, and 40 percent, respectively. The last column of data in Table 2 shows the percentage removal at equal carbon weights of 172.4g, the weight of Carbon 4 used. Once again, Carbon 4 was superior, with 78 percent removal. Carbons 1 and 3 were very similar, with 56 and 57 percent removal respectively. The removal of chloroform by Carbon 2 was 36 percent.

In Figure 2 the scale of the Y axis does not show that Carbon 4 allowed a continuous low level passage of chloroform before the major breakthrough at 28 days. This continuous low level passage averaging 1 µ g/L is shown in Figure 3. Since the surface of this GAC (made from a hydrocarbon resin) is hydrophobic and there is a higher percentage of surface area in the smaller diameter pore range than in the other types of GAC, the manufacturer recommended boiling the carbon in water to deaerate it. This was not done for the initial test. Towards the end of the 59-day test period another column was placed in service using boiled Carbon 4 GAC. Low level passage of chloroform through this column is shown in Figure 3. The average passage was again 1 µ g/L indicating that deaeration did not affect the level.

In the previous work on Miami water, it was determined that the most economical use of GAC was on finished water because it had the lowest total organic loading. Finished water normally leaves the plant with 3 mg/L of free chlorine and a total HOC level in the 185 µg/L range. The free chlorine reacts with precursor substances still present in the water after it leaves the plant, dropping to zero in less than 24 hours. Occasionally the decline in the amount of free chlorine takes up to two days. The growth of additional THM in the distribution system raises the level of total HOC at the consumer's tap to more than 300 µg/L.

If GAC were used on finished water from the clearwell before the water leaves the plant, in order to remove HOC and THMFP substances and limit the level of TTHM at the consumer's tap to not more than 100 µg/L, several problems would be encountered. Carbon removes all free chlorine so that the

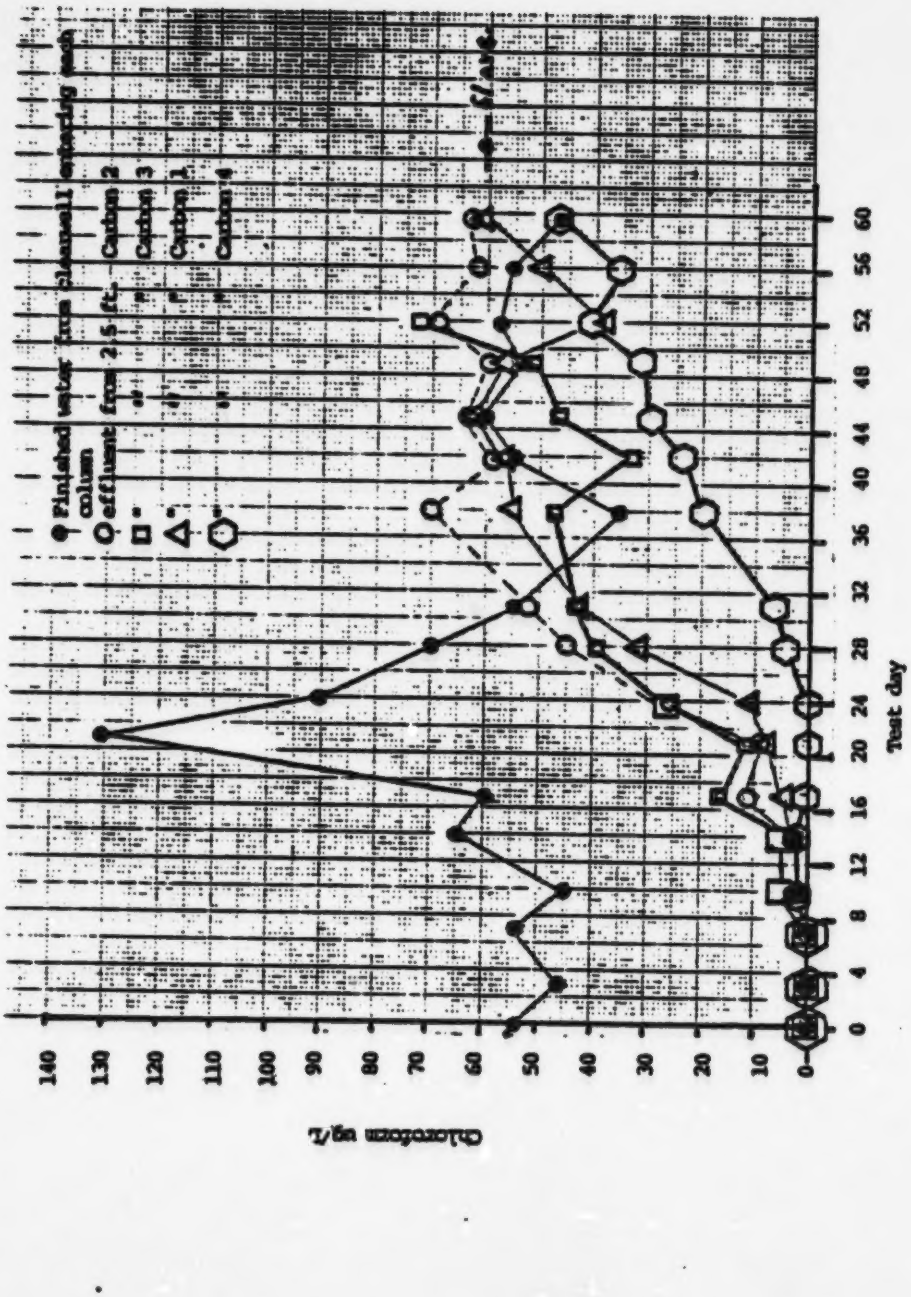


Figure 2 Chloroform breakthrough curves through Four types of GAC

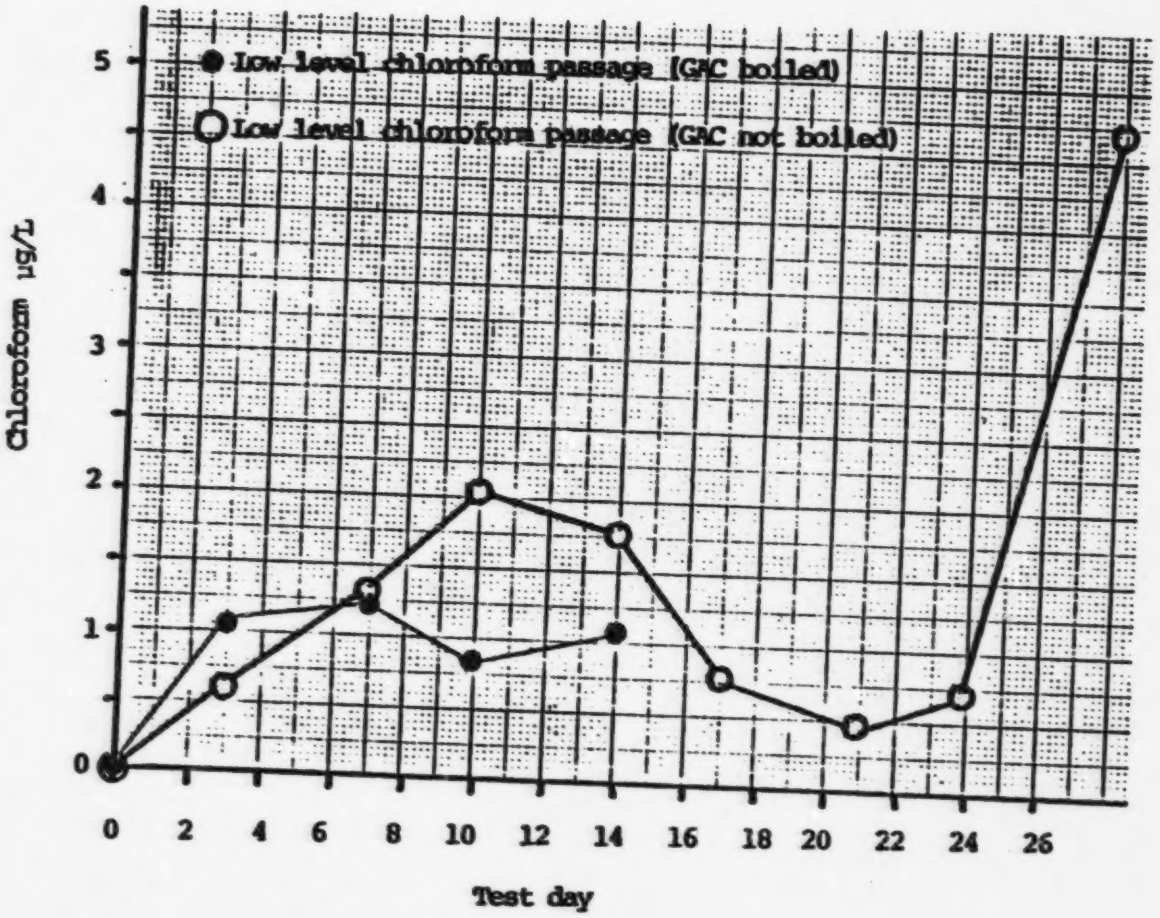


Figure 3 Low level passage of chloroform through GAC No. 4 before major breakthrough at 28 days.

effluent from a GAC column would have to be rechlorinated back to 3 mg/L of free chlorine to meet current state requirements**. Rechlorination would also be necessary because of the high bacterial count in the GAC effluent.

In this bench-scale study of the four GAC types, the relative performance was based on bed life exhaustion criteria presented in Ref. 6 and on the total TOC and THMFP substances removed over the full 59 day test period. In Ref. 6, it was noted that the GAC column was exhausted when TOC and THMFP breakthrough reached approximately 3 mg/L and 200 µg/L respectively. At this level of breakthrough, rechlorination to 3 ppm of free chlorine resulted in THM growth (two days) to the 100 µg/L level. Hereafter in this report, this will be referred to as "Criterion 1" basis of bed life exhaustion. Criterion 1 was the major factor in determining relative performance, especially THMFP removal. In this section of the work, performance was also based on the total TOC and THMFP removal in the full 59 day test run.

### A113 THMFP Removal

In Figure 4, the THMFP concentration in finished water entering columns containing four types of GAC and the THMFP breakthrough curves for each carbon are plotted. Adsorption by the four carbons was compared at two points. The curves were integrated at the end of the 59 day test period and at a THMFP breakthrough level of 200 µg/L, the point of bed failure for 2.5 ft. of GAC. At 200 µg/L THMFP breakthrough, the bed life for Carbon 1 was ten days, for Carbon 2 less than seven days, for Carbon 3 less than three days, and for Carbon 4 approximately one day. Although Carbon 4 was the best carbon for HOC removal, it was the poorest for THMFP removal. A comparison of the adsorption of each carbon at approximately ten days is made in Table 3.

TABLE 3
THMFP ADSORBED BY EACH CARBON IN
APPROXIMATELY TEN DAYS*

| Type of GAC | Equal Volume g | THMFP Adsorbed mg | Percentage THMFP Removed BY Equal Volume Of GAC | Weight Required To Adsorb As Much As 163 g Carbon 1 g | Percentage THMFP Removed By Equal Weight Of GAC (163 g) |
|---|---|---|---|---|---|
| Carbon 1 | 163 | 92.6 | 54 | | 54 |
| Carbon 2 | 195.6 | 60.3 | 35 | 300 | 29 |
| Carbon 3 | 144.1 | 23.7 | 14 | 563 | 16 |
| Carbon 4 | 172.4 | 15.1 | 9 | 1057 | 8 |

* THMFP entering in approximately ten days = 172 mg

---

**Free chlorine levels in finished water vary according to individual state requirements.

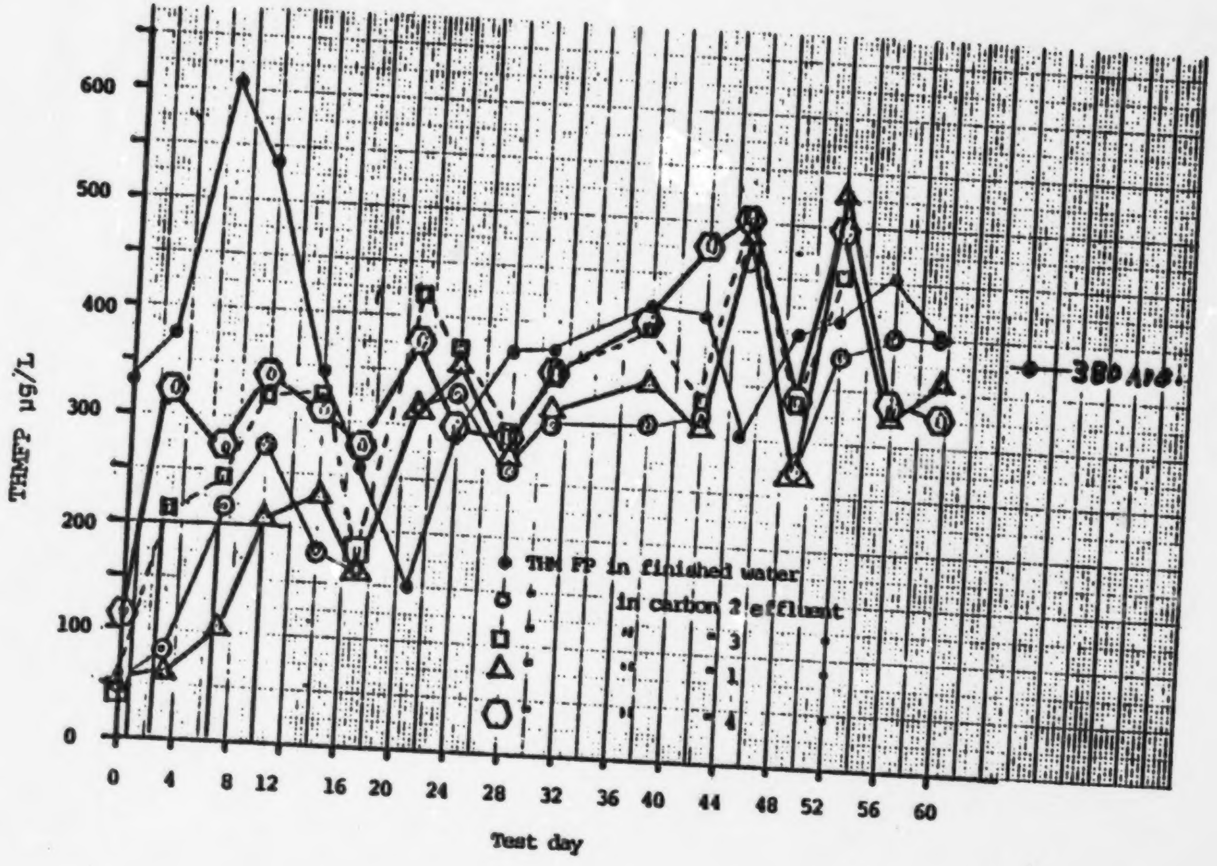


Figure 4 THMFP breakthrough curves through 4 types of GAC on Finished Water

In Table 3, the weight of each carbon required to give an equal volume in the 1 inch diameter glass columns by 2.5 ft. bed depth, is shown. Integration of the curves in Figure 4, knowing the average influent level of THMFP and total volume of water through each column, yield the THMFP (mg) adsorbed by each carbon in ten days (Table 3). Also, the percentage THMFP removed by an equal volume of GAC is shown. In ten days, Carbon 1 adsorbed the most THMFP, 163 grams of Carbon 1 adsorbed 92.6 mg of THMFP, which was 54 percent of the THMFP entering. The weight of the other carbons required to adsorb as much THMFP as 163 grams of Carbon 1 is also shown in Table 3. Also, the percentage of THMFP removal by an equal weight (163 grams) of GAC is shown. Carbon 1 was clearly the best GAC for THMFP removal on our system. In Table 4 the amount of THMFP adsorbed by each carbon column in 59 days is shown.

### TABLE 4

### THMFP ADSORBED BY EACH CARBON IN 59 DAYS*

| TYPE OF GAC | Equal Volume g | THMFP Adsorbed mg | Percentage THMFP Removed By Equal Volume Of GAC | Weight Required To Adsorb As Much As 163 g Carbon 1 g | Percentage THMFP Removed By Equal Weight Of GAC (163 g) |
|---|---|---|---|---|---|
| Carbon 1 | 163 | 524 | 26 | | 26 |
| Carbon 2 | 195.6 | 545 | 27 | 188 | 23 |
| Carbon 3 | 144.1 | 314 | 16 | 240 | 18 |
| Carbon 4 | 172.4 | 160 | 8 | 565 | 8 |

*THMFP entering in 59 days = 2002 mg

Table 4 compares the carbons at equal volume and the adsorption on an equal weight basis, compared to the 163 g weight of Carbon 1.

At 59 days 2002 mg of THMFP entered each column. The weight of each carbon is shown in Table 4. Carbon 1 adsorbed 524 mg, Carbon 2, 545 mg, Carbon 3, 314 mg, and Carbon 4, 160 mg. The last column of data in Table 4 shows the number of grams of each carbon required to adsorb as much as 163 g of Carbon 1. The required weight of Carbon 2 was 188 g (163 g of Carbon 2 would adsorb 454 mg). The required weights for Carbons 3 and 4 were 240 and 565 g, respectively. Again, Carbon 1 was preferred on our system.

### A114 TOC Removal

While TOC removal is less important to this study, THMFP removal being the primary concern, the relative performance of TOC removal by the four carbon types is important. TOC breakthrough curves are plotted in Figure 5. Based on Criterion 1 for bed life, breakthrough of approximately 3 mg/L of

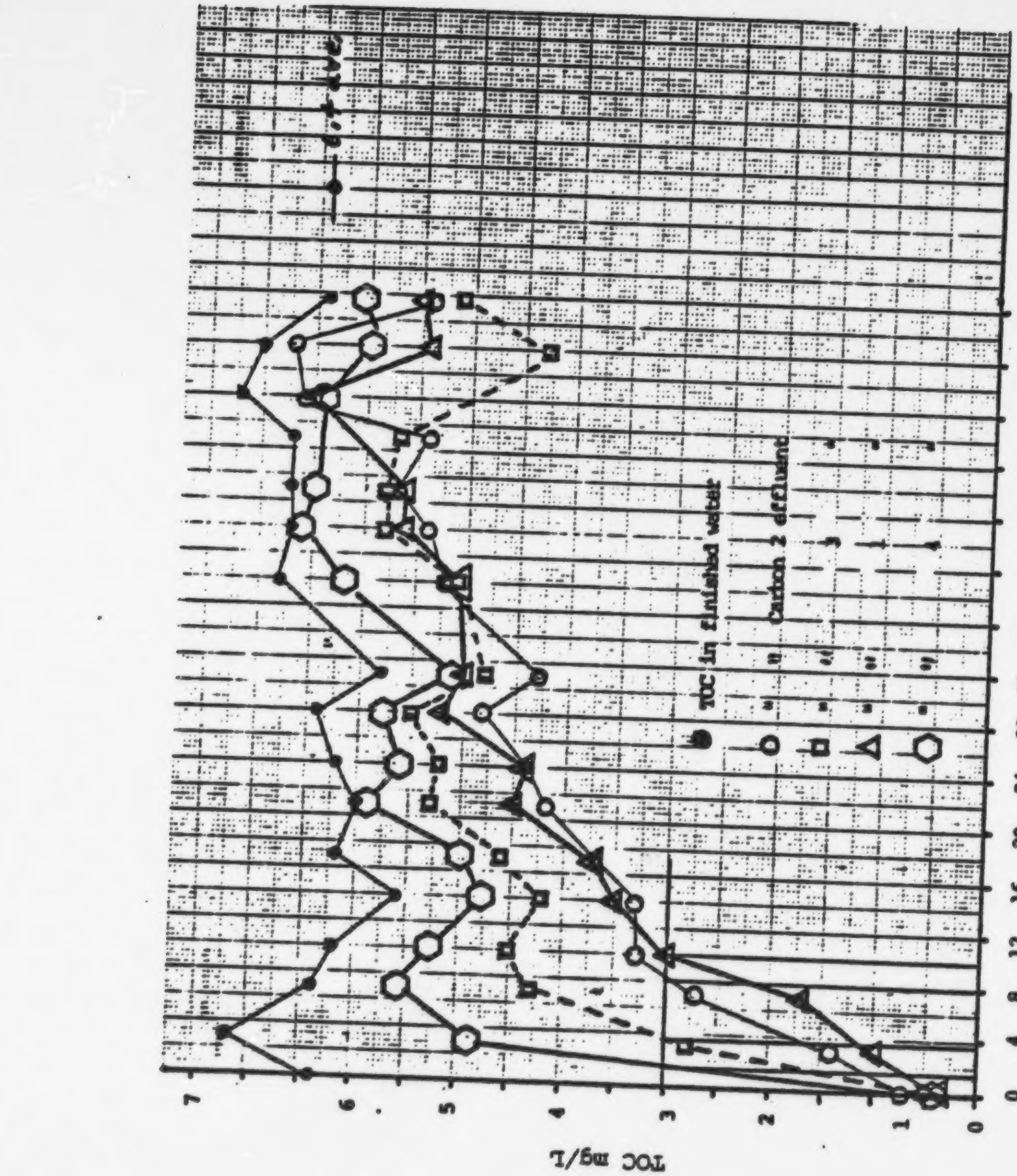


Figure 5 TOC breakthrough curves through 4 types of GAC

TOC, the bed life for Carbon 1 was 10 days, 8 days for Carbon 2, less than 4 days for Carbon 3 and approximately 1-1/2 days for Carbon 4. Again, Carbon 1 was preferred in this water system, based on TOC removal.

### A115 Carbon 1 Bed Life

In Ref. 6 it was shown that bed life based on Criterion 1 could result from solely THMFP breakthrough, or a combination of TTHM and THMFP breakthrough. In this bench scale study of the four GAC types on finished water, the reason for a bed life of 10 days for Carbon 1 (Figure 5) can be determined. For this bench scale study the daily level of TTHM in the finished water entering the GAC columns is shown plotted in Figure 6. The TTHM growth (finished water bottle aged two days) and TTHM breakthrough are also plotted. Also plotted was the TTHM growth of the GAC effluent when rechlorination to 3 ppm of free chlorine and aged two days. It is clear from Figure 6, that at the bed life of 10 days, failure was due almost entirely to THMFP breakthrough. If the THMFP substances were completely removed, bed life failure by TTHM breakthrough would have occurred at test day 35 (100 μg/L of TTHM in GAC effluent).

## A12 Bacteriological Parameters

### A121 Sampling

During the experiments using bench models, sampling of the effluent was done twice weekly. Carbon granules were sampled only once at the end of the initial experiment to avoid perturbation of the bacterial population. In subsequent bench model experiments, sampling of the carbon was done weekly.

Samples of effluent and carbon were taken aseptically in sterile polyethylene sample bags from the same sample ports used in chemical analyses. Sterile thiosulfate solution was added to samples containing residual chlorine. The samples were placed in an insulated cooler at 4°C for transport to the laboratory where they were processed within two hours. Fig. 7 is a flow diagram of the bacteriological analyses performed.

### A122 Primary Cultures

Fig. 8 shows culture procedures used. Bacteria population sizes were estimated as Total Plate Count/mL (TPC), which is a modification of the Standard Methods (Ref. 10) Standard Plate Count, and was developed in our laboratory after comparison of several plating methods and media to optimize recovery of numbers and varieties of bacteria commonly found in local soils, sediments waters. Table 5 lists the methods that were evaluated prior to accepting TPC as the method of choice for this work.

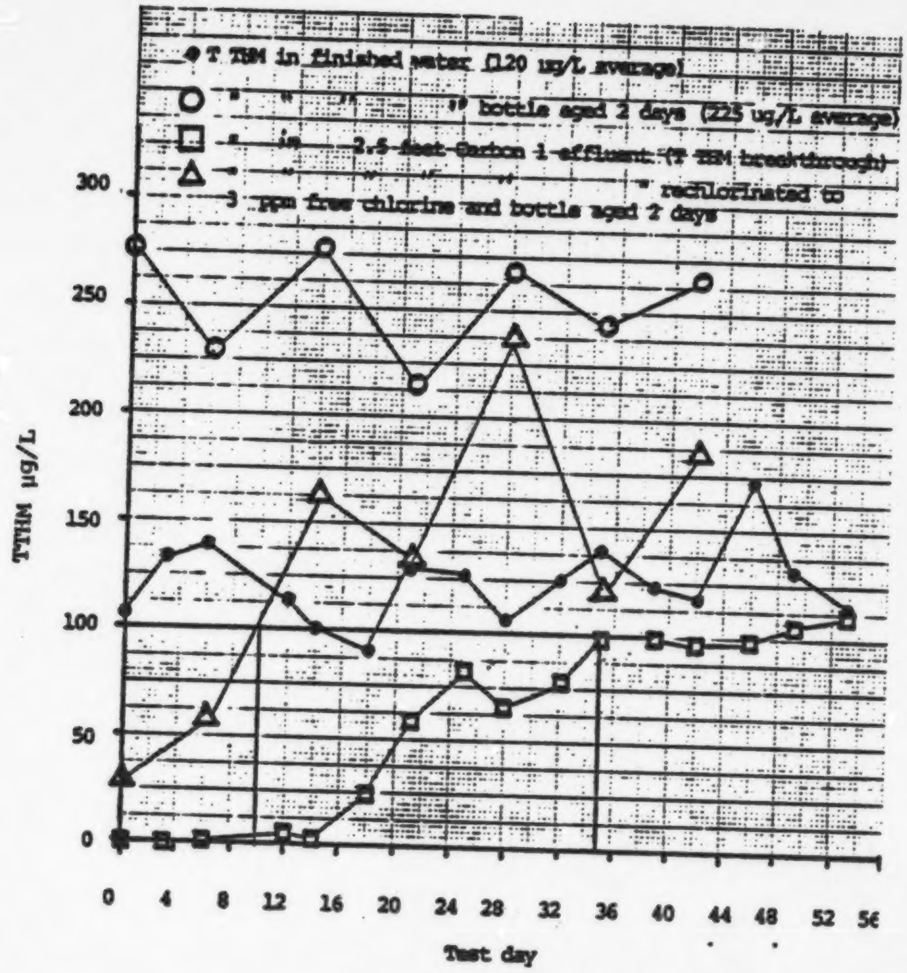


Figure 6 Bed life of 2.5 ft. of Carbon 1

For Each sample location on Flow Diagram of Pilot Plant
(or Bench-scale Model), each sample date

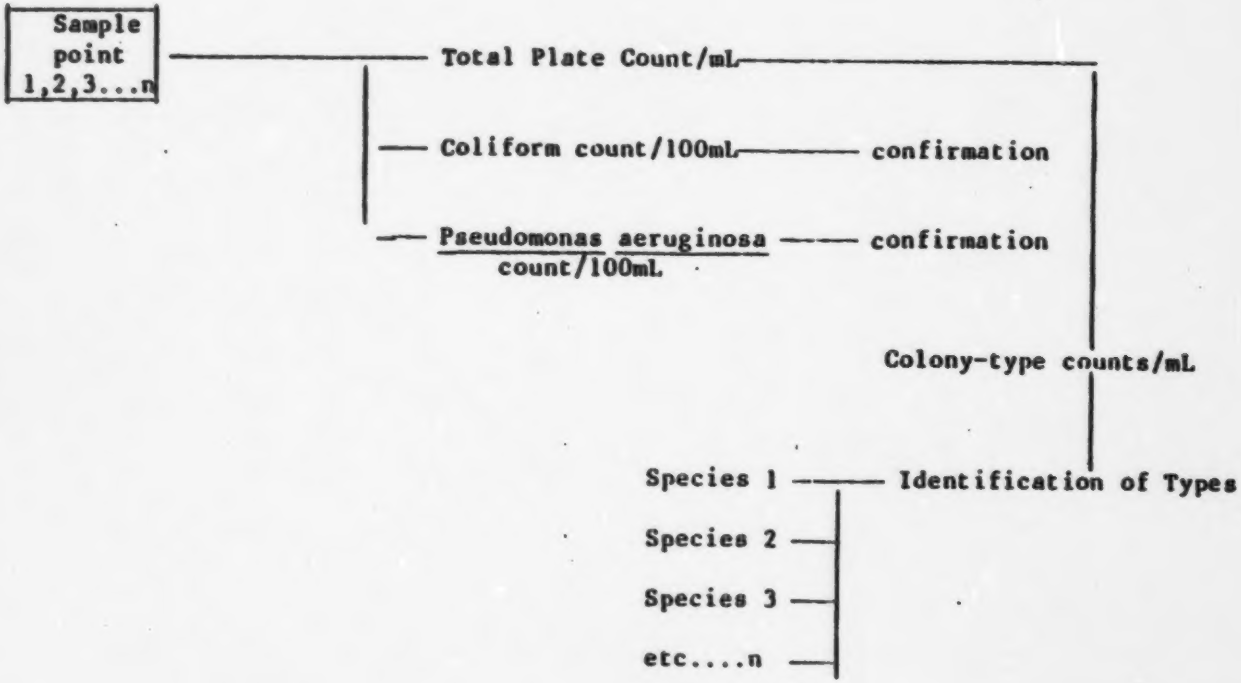

Sample point 1,2,3...n
Total Plate Count/mL
Coliform count/100mL
confirmation
*Pseudomonas aeruginosa* count/100mL
confirmation
Colony-type counts/mL
Identification of Types
Species 1
Species 2
Species 3
etc....n

Figure 7 Flow diagram of bacteriological analyses

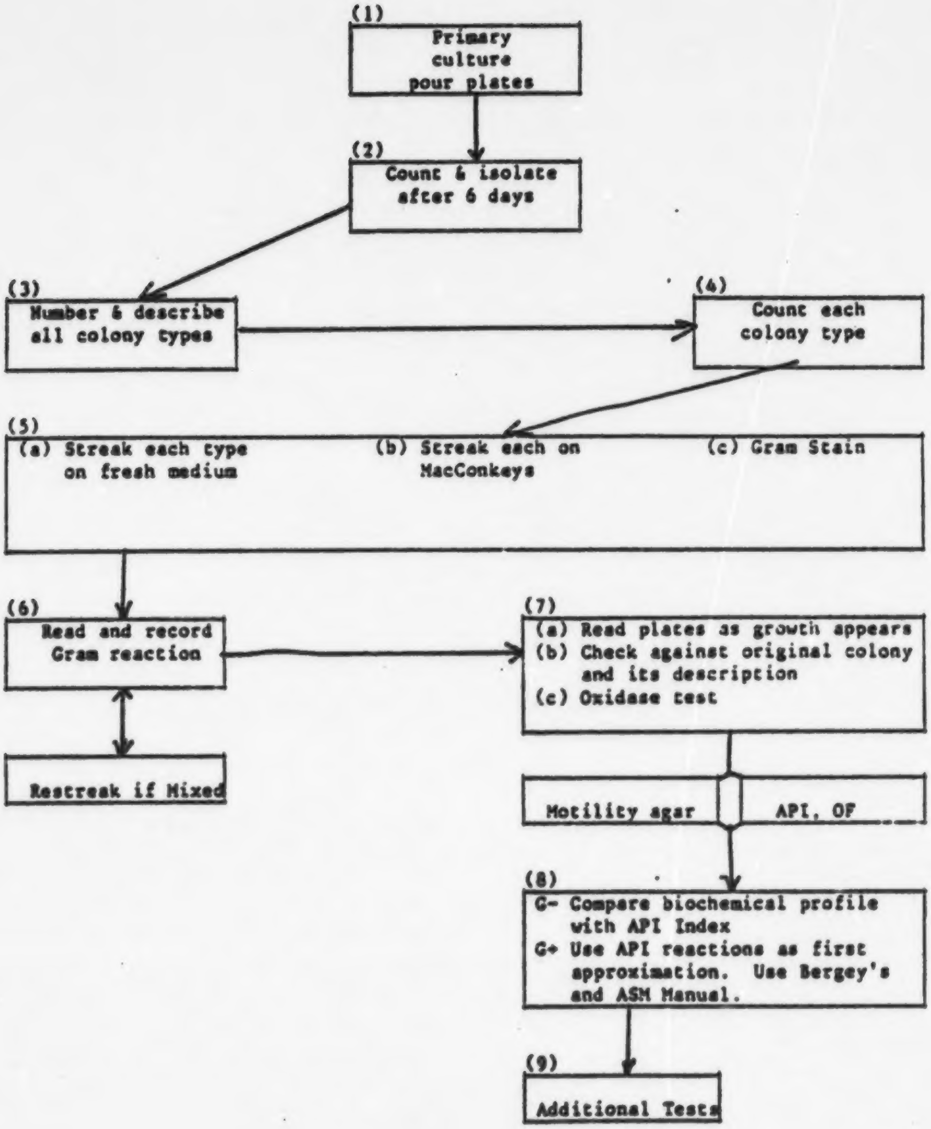

(1)
Primary culture pour plates
(2)
Count & isolate after 6 days
(3)
Number & describe all colony types
(4)
Count each colony type
(5)
(a) Streak each type on fresh medium
(b) Streak each on MacConkeys
(c) Gram Stain
(6)
Read and record Gram reaction
Restreak if Mixed
(7)
(a) Read plates as growth appears
(b) Check against original colony and its description
(c) Oxidase test
Motility agar
API, OF
(8)
G- Compare biochemical profile with API Index
G+ Use API reactions as first approximation. Use Bergey's and ASM Manual.
(9)
Additional Tests

Figure 8 Flow chart of methods used to quantify, isolate, and identify water bacteria

## TABLE 5.

## METHODS EVALUATED FOR DETERMINING TOTAL PLATE COUNTS OF BACTERIA

| Medium | Special Conditions | Incubation Time, Days | Incubation Temp., °C |
|---|---|---|---|
| Standard Methods Agar | Pour Plates | 2, 4, 6, 8, 10 | 25, 30, 35 |
| | Spread plates | 2, 4, 6, 8, 10 | 25, 30, 35 |
| | 1/2 conc. + agar added to 1.5% | 2, 6 | 30,35 |
| | 1/4 conc. + agar added to 1.5% | 2, 6 | 30, 35 |
| Brain Heart Infusion | pour & spread plates | 2, 4 | 35 |
| Czapek Agar | pour plates, membrane filter | 2, 4, 6, 10 | 25, 30, 35 |
| Starch Casein Agar | pour plates, membrane filter | 2, 4, 6, 10 | 25, 30, 35 |
| Soil Extract Agar | pour and spread plates membrane filter | 2, 4, 6, 10 | 25, 30, 35 |
| R2A Medium | pour plates, membrane filter | 2, 4, 6, 10 | 25, 30, 35 |

Duplicate dilutions and pour plates that were used in the TPC method were as described in Standard Methods (Ref. 10), but R2A medium (Ref. 11) was used instead of Standard Methods Agar (SMA) and the plates were incubated at 35°C for six days instead of 48 hours prior to counting colonies and isolating bacteria for identification. This method yielded higher counts and a greater variety of bacteria than other methods tried.

Total coliform counts were made according to the membrane filter (MF) technique described in Standard Methods. Sheen colonies were Gram stained and subcultured on nutrient agar slants for the oxidase test prior to confirmation in API strips (Analytab Products, Plainview, N.Y.).

Pseudomonas aeruginosa assays were performed according to the Standard Methods MF technique for swimming pool water using M-PA-B and confirmed in API strips.

### A123 Identification

Each colony of each colony type observed on TPC plates was counted. Four colonies of the dominant colony type and at least one of each of the remaining types on the plate chosen for the TPC from the several dilutions (at least two) made were subcultured by streaking on fresh R2A medium to isolate pure colonies. Selected colonies of these were Gram stained, examined for morphological purity, and compared with the original colony. Apparently pure Gram-negative cultures were then streaked on MacConkey's agar and motility medium, and tested for the presence of oxidase. All were put into API strips and API OF medium according to the manufacturer's instructions.

Gram negative rods were identified on the basis of their biochemical profile compared with the listings in the API Index. Additional tests were performed according to API recommendations when necessary or when suggested by the Manual of Methods of General Microbiology and the Manual of Clinical Microbiology, both published by the American Society for Microbiology, Washington D.C.

### A124 Carbon

Ultra sound was used to detach bacteria from the surfaces of granular activated carbon (GAC) in Pilot Plant experiments when it became evident during bench-scale experiments that shaking GAC in dilution water blanks was not an adequate method for recovering bacteria from these samples. A Fisher Sonic Dismembrator, Model 300 (manufactured by Artek Systems Corporation) with a maximum output of 98% of the rated 300 acoustical watts at 20 $KH_Z$ $400H_Z$ was used at 60% relative output for four minutes. The samples of GAC were held in sterile dilution water in culture tubes in an ice water bath. This method yielded the greatest number and variety of bacteria of several methods tried. Methods for recovering bacteria from GAC that were tried are listed in Table 6, and described in detail in the following section.

## TABLE 6

## METHODS EVALUATED FOR DETACHING BACTERIA FROM GAC

| |
|---|
| Weighed sample shaken twenty-five times through 2-ft. arc in dilution water blank. |
| Sample ground 1 minute in metal knife blender (Sorvall Omni Model 17105). |
| Sample pulverized in Teflon-in-glass tissue grinder (Potter-Elvejhem type). |
| Sample shaken in dilution blank as above, but with 1% v/v Triton X-100 (Rohm and Haas) added. |
| Sonication in cooled dilution water, time and intensity varied to select best. |

### A125 Methods Evaluated to Enumerate and Isolate Bacteria from Carbon Granules

In attempting to compare the numbers and kinds of bacteria that grow on carbon granules with those cultured from carbon bed effluents, highly variable results between methods were found and method reproducibility was poor. Shaking the used carbon in dilution water was suspected of inadequately washing off the adhering bacterial cells. Grinding in a Waring blender or with a tissue grinder was suspected of macerating the cells. Early suspicions of toxic substance release from GAC by grinding were examined. The decreased numbers of bacteria recovered after grinding were suspected to be caused by bacterial reattachment to newly made carbon surfaces or by mechanical precipitation (coprecipitation) of bacterial cells with the carbon as it settled. Greater colony numbers obtained from sonication of the used bed carbon probably represents more realistic numbers of the bacterial cells present.

Plating an entire subsample of carbon ground in a tissue grinder gave lower counts than shaking with dilution water and it was suspected that many bacteria attached to each carbon particle. Thus the plate count obtained was a carbon granule count rather than the bacterial population count, unless of course, some of the fine carbon particles were sterile in which case the count obtained represented neither.

Van der Kooij (Ref. 12) reported that SEM micrographs showed bacteria to be sparsely distributed on carbon surfaces with about one percent of the area occupied. If rod-shaped bacteria are assumed to have average dimensions of 0.5 x 1 micrometer (Ref. 13) each cell would cover 0.5 x $10^{-6}$ $m^2$ on a surface. One GAC granule averages 1 x 2 mm in size (average of 300 measurements). If it is assumed to be a regular cube, it would have a minimum surface area of 12 $mm^2$. There is an average of 1500 grains of GAC per gram dry weight (average of 3 grams counted) with a surface area of approximately 18,000 $mm^2$. These values are one-half as great for GAC on a wet weight basis. The greatest bacteria count obtained from used GAC was 90 x $10^6$/gram wet weight, or approximately one cell per 100 $mm^2$. GAC, of course, has a much greater surface area than that calculated for regular cubes because it has uneven surfaces and fissures.

## Experiments Performed

In the following series of experiments, granular activated carbon (GAC) used in water treatment beds and new unused carbon was examined for its 1) properties for adsorbing bacterial cells, 2) coprecipitation of bacterial cells by settling during the bacterial plating process, and 3) releasing bacteriostatic substances.

Used GAC was 1) shaken in dilution water blanks, 2) shaken in dilution water blanks with 1 percent Triton X-100 added, 3) ground with a steel knife blender, 4) ground in a tissue grinder, and 5) sonicated in dilution water. E. coli and a carbon bed isolate, Ps. Y-9-3, were mixed with new, unused GAC and recovered using the above methods. Techniques and materials used were as follows:

Dilution water was made according to Standard Methods. Triton X-100 was obtained from Rohm and Haas. E. coli, ATCC #25922, was obtained as Bactrol disks from Difco. Ps. Y-9-3, a yellow pseudomonad, was isolated from a carbon bed effluent in an earlier phase of this work. Bacterial cultures were grown on R2A medium and suspensions of cells were made in dilution water for inoculating the GAC. Suspensions were always plated prior to testing with GAC to establish beginning concentrations. The GAC tested was Filtrasorb 400 produced by Calgon Corporation, chosen as most effective in HOC and THM-FP removal in local water (Ref. 1). The metal knife blender used was a Sorvall Omni Model 17105. During grinding for 5 minutes at high speed, the blender vessel was immersed in an ice water bath. The tissue grinder was a Potter Elvehjen teflon type from Seaton Scientific Company. Sonication of GAC was performed using a Fisher Sonic Dismembrator Model manufactured by Artek Systems Corporation, Farmingdale, N.Y., and is rated at 300 watts, 98% of which is transferred as acoustical energy at 20 $KH_2$ ± 400 cycles/sec.

## Recovery of Bacteria Added to GAC, Shaking and Grinding

The purpose of this experiment was to examine 1) the effect of GAC on a bacterial cell suspension, 2) the effect of grinding the GAC on bacterial recovery, and 3) the effect of settling of carbon in the dilution blank on plate counts.

A suspension of E. coli was made in dilution water, shaken and plated. Washed new GAC was added (1 percent w/v) and the suspension was again shaken and plated. The same suspension was then ground in a steel knife blender vessel in an ice bath, shaken and plated again.

Results are given in Table 7. The decrease in counts after grinding prompted experiments to detect released bacteriostatic substances. Also suspected was coprecipitation of the bacteria with the fine carbon particles.

As the trials progressed, the speed of completion of each step probably increased and less settling time passed. The concentration of bacteria in later trials was also greater than in initial trials, which may have affected recovery. The counts obtained in the last two trials agree most closely with the initial suspension concentration, but vary by more than five percent at best. As the simplest method; i.e., shaking GAC with dilution water and plating as soon as possible, gave results that differed from that obtained from the original suspension by no more than the results obtained by grinding, we used the simpler method. The difference in results of the grinding method from the original was greater than 23 percent in the fifth trial and almost 6 percent in the sixth trial. The shake method counts varied by 23 percent from the original suspension in the last two trails, and agreed with the grinding method counts within 8 percent in the fifth trial.

The test bacterium, chosen for ease of culture, was *E. coli*, which is not a common inhabitant of water or carbon beds. It does not necessarily have the same characteristics of growth, attachment or resistance to displacement possessed by the bacteria that grow in carbon beds. Slime formers are more apt to stick to carbon surfaces. *E. coli*, however, is a small, flagellated bacterium and small cells can be expected to lodge in crevasses and pits easily and produce colonies that are securely attached to protected surfaces. *E. coli* is similar in size and shape to many of the genera isolated, i.e., *Alcaligenes* and *Pseudomonas*.

## Effect of Grinding on Recovery of Bacteria from GAC

In order to examine the possibility of bacteria adhering to new surfaces of GAC created by grinding, virgin GAC was washed in distilled deionized water. Half of it was ground in a metal knife blender in distilled deionized water. Bacterial cell suspensions of known concentration were added to each portion of the GAC in dilution water blanks, shaken, and the supernatant plated. Then each portion was again ground, which resulted in grinding the ground portion twice, and plated again. Results, shown in Table 8, indicate that the bacteria either adhered to newly exposed surfaces or were quickly precipitated out of suspension by the settling carbon particles.

Each step (Table 8) shows variable degrees of reduction in the plate count/mL, but the overall reduction was almost the same; i.e., 98 percent and 96 percent respectively for unground and ground GAC. Adding the finer GAC particles (more surface area) to the bacterial cell suspension reduced the counts more than the larger particles (Step 2, 79 percent and 17 percent reduction, respectively). Grinding alone had less effect (Step 3), with 98 percent and 80 percent reduction, respectively.

## TABLE 7

## RECOVERY OF BACTERIA (E. COLI)* FROM GAC BY SHAKING AND GRINDING

| TRIAL | DILUTION WATER + E.COLI | DILUTION WATER + E.COLI + GAC, SHAKEN | DILUTION WATER + E.COLI + GAC, GROUND | DILTUION WATER + E. COLI + GAC, SHAKEN, GROUND | |
|---|---|---|---|---|---|
| | | | | Suspension | Supernate |
| 1 | 300,000* | 30,000 | 0 | | |
| 2 | 500,000 | 0 | 0 | | |
| 3 | 790,000 | 750,000 | 110,000 | | |
| 4 | 880,000 | 1,200,000 | | 160 | 0 |
| 5 | 890,000 | 1,300,000 | | 1,200,000 | 1,100,000 |
| 6 | 1,700,000 | 1,300,000 | | 1,600,000 | 1,800,000 |

*Colony counts/mL.

## TABLE 8.

## EFFECT OF GRINDING ON RECOVERY OF BACTERIA FROM GAC.

| | | Plate count/mL obtained from Supernatant (1 g d.wt. GAC per 100 mL dilution water) | |
|---|---|---|---|
| | | Treatment #1 | Treatment #2 |
| Inoculum Treatment | Step | Washed Unground GAC[a] | Washed Ground GAC[b] |
| Dilution Water + *E. coli* (No GAC) | 1 | 460,000 | 360,000 |
| | | 17%[d] | 79% |
| Dilution Water + *E. coli* + GAC | 2 | 98% 380,000 | 96% 75,000 |
| | | 98% | 80% |
| Dilution Water + *E. coli* + GAC + Grinding[c] | 3 | 7,800 | 15,000 |

[a] 0.0044g decanted off in supernatant wash water

[b] 0.0086g decanted off in supernatant wash water

[c] This resulted in grinding the ground GAC twice

[d] Percentage reduction in plate count/mL caused by subsequent step

## Bacteriostatic Substances

The release of bacteriostatic substances from GAC was examined in two ways, both dependent on dose-response effects. In the first experiment, 10 percent, w/v, virgin GAC in dilution water was shaken for 30 minutes to elute possible bacteriostatic substances. Two-fold dilutions (with dilution water), in 9.9 mL volumes, from undiluted to 1:128 of the eluate were inoculated with 0.1 mL of a culture suspension containing approximately 50,000 cells per mL of 1) E. coli and 2) Y-9-3, a carbon effluent isolate from an earlier study. The cells were distributed by shaking and 1 mL of each resulting suspension plated in R2A. The plates were incubated at 35°C. The E. coli cultures were read after 48 hours; the Y-9-3 cultures were read after six days. The results are shown in Table 9. In the second method, a 10 gram sample of virgin GAC was washed ten times sequentially with 100 mL volumes of distilled water. To each of these 100 mL washes, 1 mL of a suspension containing approximately 50,000 cells per mL of each of the test bacteria was added, shaken, and plated. Results are shown in Table 10.

In both cases the variability in plate counts obtained with E. coli as the test organism was approximately that to be expected from duplicate plates made from one sample (Tables 9, 10). The Ps. Y-9-3 isolate gave comparable counts in the sequential wash test. The variability was greater for Ps. Y-9-3 counts obtained in the eluate dilution test, but the variability occurred erratically in the dilution sequence and was not dose related (Table 9). It was therefore concluded that no bacteriostatic substances had been eluted from the GAC by dilution water.

## Sonication vs. Shaking

Sonication and shaking in dilution water were compared as methods for recovering bacteria from GAC surfaces. One gram samples of GAC from a used filter bed were placed in 2 mL sterile dilution water in culture tubes and sonicated for 1, 5, and 10 minutes at 10, 20, 30, 35, 40, 50, and 60 percent relative output.

Results shown in Table 11 were averaged values of three experiments and indicated that greater bacteria counts were obtained from samples sonicated at 60% relative output than at lower levels. From $3.7 \times 10^6$ to $1.1 \times 10^7$ TPC/mL were obtained from sonicated samples and from $8.0 \times 10^3$ to $2.0 \times 10^4$ were obtained from samples shaken in dilution water (Table 11 (A)).

When output was held constant at 60% and time was varied, sonication for 2-4 minutes yielded the highest counts (Table 11) (B)). Sonicated samples yielded TPC/mL that were from 4 to over 600 times greater than those obtained by shaking GAC in dilution water.

Table 12 lists the kinds of bacteria that were isolated and identified from sonicated and shaken GAC samples. Not only were the numbers of bacteria recovered from sonicated samples greater than from shaken samples, but more

# TABLE 9

## DETERMINATION OF BACTERIOSTATIC EFFECT OF DILUTED GAC ELUATE (DOSE/RESPONSE).

| | Plate Count/mL | |
|---|---|---|
| Treatment | Ps. Y - 9 - 3 | E. coli |
| Culture suspension in dilution water | 1500 | 2000 |
| Culture + undiluted eluate | 2000 | 2100 |
| Culture + eluate 1:2 | 2100 | 1900 |
| 1:4 | 2000 | 2000 |
| 1:8 | 1900 | 1800 |
| 1:16 | 1400 | 1900 |
| 1:32 | 1500 | 2000 |
| 1:64 | 1400 | 1700 |
| 1:128 | 1900 | 2000 |
| $\overline{x}$ | 1744 | 1933 |
| s.d. | 287 | 122 |
| C.V. | 16% | 6% |
| Range | 1400 - 2100 | 1700 - 2100 |

## TABLE 10

## DETERMINATION OF BACTERIOSTATIC EFFECT OF SEQUENTIAL ELUATES OF GAC.

| | Plate Count/mL | |
|---|---|---|
| Wash no. | Ps. Y - 9 - 3 (6 days) | E. coli (48 hrs.) |
| Dilution water cell suspension | 390 | 500 |
| 1 | 400 | 490 |
| 2 | 360 | 500 |
| 3 | 370 | 510 |
| 4 | 390 | 530 |
| 5 | 350 | 490 |
| 6 | 390 | 500 |
| 7 | 390 | 450 |
| 8 | 410 | 470 |
| 9 | 400 | 460 |
| 10 | 390 | 450 |
| $\overline{x}$ | 390 | 490 |
| s.d. | 18 | 26 |
| C.V. (%) | 4.7 | 5.3 |
| Range | 350 - 410 | 450 - 510 |

## TABLE 11

### TOTAL PLATE COUNTS/ML OBTAINED FROM USED BED GAC TREATED WITH SONICATION AND SHAKING PRIOR TO PLATING.

(A, TIME CONSTANT, OUTPUT VARIED; B, OUTPUT FIXED AT 60%, TIME VARIED.)

| (A) | | | | (B) | | | |
|---|---|---|---|---|---|---|---|
| Sonic Output, % | TIME | | | Time, Min. | Sample | | |
| | 1 min | 5 min | 10 min | | 1 | 2 | 3 |
| min | 3,400,000 | - | 300,000 | 1 | 700,000 | 3,300,000 | - |
| 10 | - | 360,000 | 480,000 | 2 | 940,000 | 4,300,000 | 5,000,000 |
| 20 | 2,100,000 | 420,000 | 540,000 | 4 | 980,000 | 120,000,000 | 6,300,000 |
| 30 | 2,400,000 | 480,000 | 600,000 | 5 | 430,00 | 2,300,000 | - |
| 35 | 2,700,000 | 900,000 | 660,000 | 6 | 580,000 | 1,500,000 | 7,200,000 |
| 40 | 3,800,000 | 950,000 | 720,000 | 8 | 370,000 | 700,000 | 8,200,000 |
| 50 | 9,000,000 | 1,200,000 | 1,800,000 | 10 | 240,000 | 400,000 | 6,000,000 |
| 60 | 11,000,000 | 1,400,000 | 3,700,000 | 12 | 230,000 | 1,100,000 | 4,000,000 |
| | | | | 14 | 380,000 | 100,000 | 3,200,000 |
| | | | | 15 | 380,000 | 83,000 | - |
| Shaken | 20,000 | 8,000 | 8,000 | Shaken | 14,000 | 20,000 | 12,000 |

a "minimum" setting

TABLE. 12

SPECIES OF BACTERIA, PLATE COUNT/mL, ISOLATED FROM SONICATED GAC (OUTPUT FIXED AT 60%, TIME VARIED) COMPARED WITH GAC SHAKEN IN DILUTION WATER PRIOR TO PLATING

| Method | Species | 1 min | 2 min | 4 min | 5 mi | 6 min | 8 min | 10 min | 12 min | 14 min | 15 min |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | USED GAC #1 | | | | | | | | | | |
| Sonication | *Acinetobacter lwoffi* | 130,000 | | | 100,000 | 260,000 | | 110,000 | 160,000 | 230,000 | 200,000 |
| | *Acaligenes* spp. | | 30,000 | | | | | | | | |
| | *Moraxella* spp. | | | | | | 10,000 | | | | |
| | Gram-positive rods | 570,000 | 910,000 | 920,000 | 310,000 | 260,000 | 340,000 | 130,000 | 70,000 | 150,000 | 180,000 |
| | Unidentified/Died | | | 60,000 | 20,000 | 60,000 | 20,000 | | | | |
| Shaken | *Acinetobacter lwoffi* | 6,000 | | | | | | | | | |
| | *Moraxella* spp. | 1,000 | | | | | | | | | |
| | Unidentified/Died | 2,000 | | | | | | | | | |
| | Gram-positive rods | 5,000 | | | | | | | | | |
| | USED GAC #2 | | | | | | | | | | |
| Sonication | *Alcaligenes* spp. | 2,700,000 | 3,800,000 | 97,000,000 | 1,300,000 | 1,100,000 | 400,000 | 360,000 | 1,100,000 | 56,000 | 83,000 |
| | Gram-positive rods | | | 5,000,000 | | | | | | | |
| | Unidentified/Died | 600,000 | 500,000 | 13,000,000 | 1,000,000 | 400,000 | 300,000 | 40,000 | | 44,000 | |
| Shaken | *Alcaligenes* spp. | 19,500 | | | | | | | | | |
| | Unidentified/Died | 900 | | | | | | | | | |

kinds of bacteria were also recovered. The first GAC sample yielded five kinds when sonicated and four kinds when shaken. The second, which was a duplicate of the first, three kinds when sonicated and two when shaken. All kinds were not recovered from each sonication time category and apparently some species were affected by longer exposure times. The effect was not uniform, however, and the data are insufficient for generalization. For example, in the first GAC sample Alcaligenes spp. apparently did not survive sonication longer than 2 min., but did survive 15 min. in the second GAC sample.

Recoveries from these two samples, which were duplicates, indicated that the bacteria were not uniformly distributed on the GAC, nor did they respond uniformly. Even well-mixed GAC samples were not homogeneous enough to provide duplicate sub-samples and it was difficult to average results from repeated experiments.

If the population of bacteria was large enough, even shaking for 1 minute allowed recovery of a variety of kinds, but sonication yielded greater numbers and more often a greater variety of kinds.

### A126 Quality Assurance

The qualities of laboratory results, procedures, equipment performance, and materials were monitored according to the laboratory Quality Control Manual, which is based on that outlined in Microbiological Methods for Monitoring the Environment (Robert Bordner, John Winter, and Pasquale Scarprino, Editors. 1978. EMSL, US, EPA publication EPA-600/8-78-017, Cincinnati, OH. Logs were kept of all laboratory equipment performance and work.

### A127 Results

Results of this phase, comparison of four GAC's effluents, are shown in Tables 13 thru 16 and Figure 9. Mean ($\bar{X}$), standard deviation (s), coefficient of variation (c.v.), and range of values obtained for the Total Plate Count/mL from each sample are shown in Table 13. The total bacteria counts in the water effluent of each column are also shown graphically in Figure 9.

Dominant bacteria are listed for each sample in Table 14. Table 15 is a list of the most common bacteria, and Table 16 is a list of less common bacteria. The number of times each occurred, the range of values for count/mL, and the samples from which each was isolated are also given. Although the averages of values of counts/mL for the experimental period are indicated on the graphic representations of population sizes (Fig. 9), and given in Table 13, they have no real meaning at any given time. The variabilities of the count/mL values were so great (from 87 percent to 410 percent) as shown by the coefficients of variation (c.v.) that the mean values were only gross approximations of the dynamic state of the populations. The

# TABLE 13

## TOTAL BACTERIA COUNTS, COLONIES/mL
## ED 1, PHASE 1

| SAMPLE | $\bar{X}$ | S.D. | C.V. | RANGE |
|---|---|---|---|---|
| 1 Raw | 59,000 | 242,000 | 4.10 | 2 - $10^6$ |
| 3 H.T. | 68,000 | 242,000 | 3.54 | 15 - $10^6$ |
| 5 Finished | 15 | 26 | 1.73 | 0 - 85 |
| 7 WVG | 38,000 | 36,000 | 0.93 | 5,000 - 130,000 |
| 9 ICI | 37,000 | 35,000 | 0.94 | 300 - 130,000 |
| 11 F400 | 81,000 | 123,000 | 1.51 | 1,000 - 500,000 |
| 13 W950 | 43,000 | 37,000 | 0.87 | 3,000 - 100,000 |

## TABLE 14

## DOMINANT ORGANISMS FOUND IN EACH SAMPLE
## ED 1, PHASE 1

| | |
|---|---|
| 1 Raw | *Acinetobacter*, *Alcaligenes*, *Moraxella*, *Pseuodomonas*-like |
| 3 H.T. | *Acinetobacter*, *Alcaligenes*, *Moraxella*, *Pseuodomonas*-like |
| 5 FW | *Acinetobacter*, *Alcaligenes*, Gram + Rods, *Staphylococcus*, *Torula* |
| 7 - 13 GAC | *Acinetobacter*, *Alcaligenes*, Gram + Rods, *Moraxella*, *Pseudomonas*-like |

## TABLE 15

## MOST COMMONLY OCCURRING BACTERIA
## ED 1, PHASE 1

| | OCCURRENCES | RANGE, COLONIES/ML | WHERE OCCURRED |
|---|---|---|---|
| *Acinetobacter* spp. | 49 | 1 - 140,000 | All samples |
| *Alcaligenes* spp. | 60 | 1 - 94,000 | All samples |
| CDC VE-2-like | 32 | 1 - 4,600 | All except fin. |
| *Moraxella* spp. | | | |
| *Pseudomonas*-like | | | |
| Oxidase + | 60 | 10 - 60,000 | All samples |
| Oxidase - | 21 | 1 - 600 | All except fin. |
| Gram + Rods | 66 | 1 - 500,000 | All samples |

## TABLE 16

## BACTERIA OCCURRING LESS FREQUENTLY
## ED 1, PHASE 1

| | OCCURRENCES | RANGE, COLONIES/ML | WHERE OCCURRED |
|---|---|---|---|
| *Achromobacter* spp. | 2 | 2,000 | 9 |
| *Aeromonas* spp. | 10 | 4 - 400 | 1, 3, 13 |
| *Pseudomonas* spp. | 14 | 10 - 90,000 | All except fin. |
| *Staphylococcus* spp. | 9 | 10 - 9,000 | 1, 5, 7, 9, 11, 13 |
| *Micrococcus* spp. | 5 | 6 - 1,000 | 1, 3, 13 |
| *Flavobacterium* spp. | 6 | 2 - 100 | 7, 9, 11 |
| *Erwinia* spp. | 1 | 1 | 1 |
| *Corynebacterium* spp. | 2 | 1,000 - 9,400 | 7, 9 |
| CDC Groups | 12 | 1 - 3,000 | 1, 3, 9, 11, 13 |
| *Torula* | 7 | 50 - 200 | 1, 3, 5, 7, 9 |
| Molds | 4 | 1 - 14,000 | 1, 3, 5, 7, 9, 11 |
| Unidentified/Died | 16 | 500 60,000 | All samples |

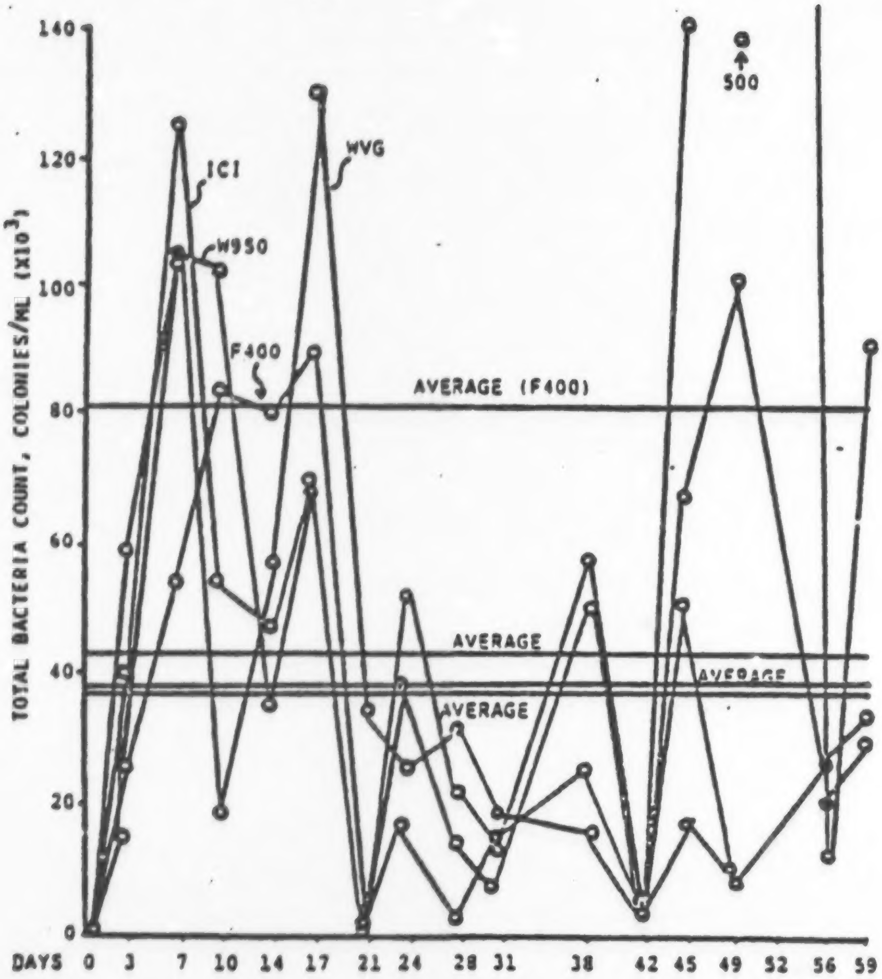


Figure 9. Four columns bacteria counts superimposed. Even without the one very high count (500,000 per mL), the mean of counts obtained from F400 samples was greater than those from the other three GAC's (68,000/mL).

range of counts examined together with the means may better indicate this dynamism.

Unlike German workers, we found great variability in the bacterial counts during the 59 days of Experiment 1. Klotz (Ref. 14) found population stability after 20 days operation of GAC beds. Cairo et al. (Ref. 15) reported that bacterial levels "decrease and level off" when the bacterial population in the GAC became "established" and reached a "pseudosteady state". Our columns exhibited a series of blooms and declines (Fig. 9).

There was no appreciable difference between three carbons, WBG, ICI, and W950. The F400 had a higher average colony count (80,000/mL) (Fig. 9,). There was a large bloom (500,000/mL) of Gram positive rods on Day 49. Even without this value, F400 had a higher mean colony count, 68,000/mL, than the other three, which had mean counts around 40,000/mL. Because the bacteria were present in greater numbers, it may only indicate that the surfaces had a greater affinity for organic molecules or the bacteria themselves rather than that the bacteria were regenerating the carbon and freeing adsorption sites. Although the columns received the same water, each developed its own pattern of increases and decreases in numbers of bacteria recovered from the effluents and carbon.

The dominant organisms were few: Acinetobacter spp., Alcaligenes spp., Moraxella spp., and Pseudomonas-like spp. These are all heterotrophs common to natural organic-laden waters. No coliforms or Pseudomonas aeruginosa were found. Table 16 lists bacteria found less frequently, range of numbers recovered, and location observed.

The differences in bacteria counts shown here may help explain the different counts and GAC behavior reported in the literature, and support the observations of Schalekamp (Ref. 16). Different GAC can be expected to behave differently in waters of different compositions as shown by the reported values for bed life, breakthrough times, and bacteria counts. This indicates the need for study of each water source with respect to its most efficacious treatment method regarding the adsorptive as well as microbiological performance.

Many different kinds of colonies developed in primary culture plates that did not grow in subculture and so were not identified. The survival rate for subcultures was 80% of all colony types picked for streaking. The colonies that did not survive the isolation and identification process are listed in all tables as Unidentified/Died and were sometimes the dominant colony type in TPC plates.

Many different kinds of colonies that grew in primary plates survived subculturing and grew in media designed to test the enzymatic characteristics of bacteria, which is the basis of their identification. These bacteria occurred frequently, but were rarely present in large numbers. They had recognizable colonial morphologies, and apparently stable biochemical characteristics, but fit no taxononic key, and were given descriptive names. As they were all Gram negative, non-spore forming rods, they are listed in the result tables as pseudomonads or Pseudomonas-like. They and their biochemical reactions are listed in Tables 17 (A) and 17 (B).

## A2 Phase 2, Bench-Scale Study of Best GAC from Phase 1 on Lime-Softened Water

### A21 Bench-Scale Unit 1

This bench-scale project was divided into two parts, 1) to study the effectiveness of the best GAC, chosen in Phase 1, to remove organic substances from lime-softened water which was recarbonated to a pH of 8.5, and 2) to study the removal of spiked organics by GAC.

#### A211 Chemical Parameters

##### A2111 Bench-Scale Unit 1 Design

A bench-scale adsorption unit, Section A of Figure 10, was set up to study the effectiveness of the best GAC, Carbon 1, in Phase 1 to remove organic substances from lime-softened water which was sand filtered and adjusted to a pH of 8.5 by recarbonation with carbon dioxide. The ozone study in the Pilot Plant would use a similar water feed to the ozone contactors and to the control BAC tower receiving non-ozonated water. The glass columns were the same as used in Phase 1. Water flow rates were the same. The total bed depth for Carbon 1 was 7 feet. In Figure 10, sampling points in the Preston Plant and Miami Distribution System are shown, as well as sampling points in the bench-scale adsorption unit. Lime-softened water from the Preston Plan was labeled Sampling Point 3. This water was recarbonated, as shown, before entering Section A. The sand column in Section A filtered the lime-softened water before entering the GAC columns. This sand column developed its own bacteria profile and its effect on TOC and THMFP could be studied.

###### A21111 THMFP Removal by GAC in Section A of Bench-Scale Unit 1

The concentration of THMFP in lime-softened water, Sampling Point 3 Section A was plotted in Figure 11. The concentration after recarbonation, Sampling Point 3A was also plotted. The average concentration over the full testing period, 63 days, was 562 µg/L and 569 µg/L for Sampling Points 3 and 3A, respectively. In this case, a comparison of data from 3 and 3A serves to show the analytical precision of the THMFP method. The average THMFP concentration from the sand column in Section A, also plotted, was 472 µg/L,

## TABLE 17 (A)

## BIOCHEMICAL REACTIONS[a] OF OXIDASE POSITIVE PSEUDOMONADS

| GROUPS AND SUBGROUPS | BIOCHEMICAL REACTIONS | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ONP | ADH | CIT | URE | VP | GEL | MAN | RHA | SAC | ARA | NO2 | N2 | MOT | MAC | CAT |
| White Cross | | | | | | | | | | | | | | | |
| 1 | – | – | – | – | + | – | – | – | – | – | – | – | + | – | – |
| 2 | – | – | – | – | + | – | – | – | – | – | – | – | + | – | – |
| 2a | | | | | – | + | | | | | | | | | |
| 3 | – | – | – | – | – | – | – | – | – | + | + | – | + | – | – |
| 4 | – | – | – | ± | + | + | + | – | – | + | + | – | + | – | – |
| 5 | – | – | – | – | + | + | + | – | – | – | + | – | + | – | – |
| 6 | – | – | – | – | – | – | – | + | – | – | – | + | + | ± | – |
| 7 | – | – | – | – | – | – | – | + | – | + | – | + | + | ± | – |
| 8 | – | – | – | – | – | + | + | – | – | + | + | – | + | – | – |
| White Sphere | | | | | | | | | | | | | | | |
| 1 | – | – | – | – | + | + | + | – | – | ± | + | – | + | – | – |
| 2 | – | – | – | – | + | – | – | – | – | – | + | – | + | + | – |
| 3 | – | – | + | + | – | – | – | – | – | – | – | – | + | ± | – |
| 4 | – | – | + | + | – | + | – | – | – | – | – | – | + | ± | – |

[a] Biochemical tests abbreviated as follows: ONPG=orthonitrophenol-galactopyranoside, ADH=arginine dihydrolase, CIT=citrate, URE=urea, VP=Voges-Proskauer, GEL=gelatin, MAN=mannitol, RHA=rhamnose, SAC=sucrose, ARA=arabinose, AMT=amygdalin, $NO_2$=nitrite, $N_2$=nitrogen, MOT=motility, MAC=MacConkey, OFO=glucose oxidation and CAT=catalase.

TABLE 17 (A) (CONTINUED)

BIOCHEMICAL REACTIONS[a] OF OXIDASE POSITIVE PSEUDOMONADS

| GROUPS AND SUBGROUPS | BIOCHEMICAL REACTIONS | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ONP | ADH | CIT | URE | VP | GEL | MAN | RHA | SAC | ARA | NO2 | N2 | MOT | MAC | CAT |
| White Lens | | | | | | | | | | | | | | | |
| 1 | + | - | - | - | - | - | - | - | - | - | - | - | + | - | - |
| 2 | + | - | - | - | - | - | - | + | + | + | - | - | + | ± | + |
| White Speck | | | | | | | | | | | | | | | |
| 1 | + | - | - | - | - | - | - | - | - | + | - | - | - | - | - |
| Rose Lens | | | | | | | | | | | | | | | |
| 1 | - | - | - | - | - | - | - | - | - | - | + | - | + | + | + |
| 2 | - | + | - | - | - | - | - | - | - | - | - | - | + | - | - |
| 3 | - | + | - | - | - | - | - | - | - | - | - | - | + | - | + |
| 4 | - | + | - | - | + | ± | - | - | - | - | + | - | + | - | - |
| Orange | | | | | | | | | | | | | | | |
| 1 | - | - | - | - | - | - | - | - | - | - | - | - | + | ± | - |
| Golden Yellow | | | | | | | | | | | | | | | |
| 1 | - | - | + | - | + | - | - | - | + | - | - | + | - | - | - |
| 2 | - | - | - | - | + | - | - | - | + | - | - | - | - | - | - |
| 3 | - | - | - | - | - | - | - | - | - | - | - | - | + | - | - |

### TABLE 17 (A) (CONTINUED)

### BIOCHEMICAL REACTIONS[a] OF OXIDASE POSITIVE PSEUDOMONADS

| GROUPS AND SUBGROUPS | BIOCHEMICAL REACTIONS | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ONP | ADN | CIT | URE | VP | GEL | MAN | RHA | SAC | ARA | $NO_2$ | $N_2$ | MOT | NAC | CAT |
| Yellow | | | | | | | | | | | | | | | |
| 1 | - | - | + | - | - | - | - | - | + | - | - | - | + | - | - |
| 2 | - | - | - | + | - | - | - | + | - | - | - | - | + | - | - |
| 3 | - | - | + | - | - | - | - | - | - | - | - | - | - | + | - |
| 4 | - | - | - | - | - | + | - | - | - | - | - | + | + | - | - |
| 5 | - | - | - | - | - | + | - | - | - | - | - | - | - | - | - |
| Roselobe | | | | | | | | | | | | | | | |
| 1 | - | - | - | - | + | + | + | - | - | + | - | + | + | - | - |
| 2 | - | - | - | - | + | + | + | - | - | - | + | - | + | - | - |
| 3 | + | - | ± | _ | - | - | - | - | - | - | + | - | + | ± | - |
| 4 | - | - | - | - | + | - | - | - | - | - | + | - | + | ± | - |
| 5 | - | - | ± | + | - | + | + | - | - | ± | + | - | + | ± | - |
| 6 | - | - | - | - | - | - | - | - | - | - | + | - | + | + | - |
| 7 | - | - | - | - | - | + | - | - | - | - | + | - | + | + | - |

## TABLE 17 (B)

### BIOCHEMICAL REACTIONS[a] OF OXIDASE NEGATIVE PSEUDOMONADS

| GROUPS AND SUBGROUPS | BIOCHEMICAL REACTIONS | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ONP | ADH | CIT | URE | VP | GEL | MAN | RHA | SAC | AMY | ARA | $NO_2$ | $N_2$ | MOT | MAC | OFO | CAT |
| **Golden Yellow** | | | | | | | | | | | | | | | | | |
| 1 | - | - | - | - | - | - | - | - | + | - | - | + | - | - | + | ak | - |
| 2 | + | - | + | - | - | + | - | - | - | - | - | - | - | - | - | - | - |
| 3 | + | - | + | - | + | + | - | - | - | - | - | - | - | - | - | - | - |
| 4 | - | - | + | - | + | + | - | - | ± | - | - | - | + | - | - | ak | - |
| 5 | - | - | - | - | - | + | - | - | - | - | - | - | - | - | - | - | - |
| 6 | - | - | - | - | - | - | - | - | - | - | - | + | - | - | - | - | - |
| 7 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | ak | - |
| **Lemon Yellow** | | | | | | | | | | | | | | | | | |
| 1 | + | - | - | - | - | - | - | + | - | - | - | - | - | + | - | - | - |
| 2 | - | - | - | - | - | - | - | + | - | - | + | - | - | + | - | - | - |
| 3 | - | - | - | - | + | - | + | - | + | + | - | - | - | + | - | - | - |
| **Yellow Cross** | | | | | | | | | | | | | | | | | |
| 1 | ± | - | - | + | + | - | - | - | + | - | - | - | - | + | - | - | + |
| 2 | ± | - | - | + | + | - | - | - | + | - | + | - | - | + | - | - | + |
| 3 | - | - | - | - | - | - | - | - | + | - | + | - | - | + | - | - | + |
| 4 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | ak | + |

[a] Biochemical tests abbreviated as follows: ONPG=orthonitrophenol-galactopyranoside, ADH=arginine dihydrolase, CIT=citrate, URE=urea, VP=Voges-Proskauer, GEL=gelatin, MAN=mannitol, RHA=rhamnose, SAC=sucrose, ARA=arabinose, AMY=amygdalin, $NO_2$=nitrite, $N_2$=nitrogen, MOT=motility, MAC=MacConkey, OFO=glucose oxidation and CAT=catalase.

TABLE 17 (B)

BIOCHEMICAL REACTIONSD[a] OF OXIDASE NEGATIVE PSEUDOMONADS

| GROUPS AND SUBGROUPS | BIOCHEMICAL REACTIONS ONP | ADH | CIT | URE | VP | GEL | MAN | RHA | SAC | AMY | ARA | $NO_2$ | $N_2$ | MOT | MAC | OFO | CAT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Golden Yellow | | | | | | | | | | | | | | | | | |
| 1 | - | - | - | - | - | - | - | - | + | - | - | + | - | - | + | ak | - |
| 2 | + | - | + | - | - | + | - | - | - | - | - | - | - | - | - | - | - |
| 3 | + | - | + | - | + | + | - | - | - | - | - | - | - | - | - | - | - |
| 4 | - | - | + | - | + | + | - | - | ± | - | - | - | + | - | - | ak | - |
| 5 | - | - | - | - | - | + | - | - | - | - | - | - | - | - | - | - | - |
| 6 | - | - | - | - | - | - | - | - | - | - | - | + | - | - | - | - | - |
| 7 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | ak | - |
| Lemon Yellow | | | | | | | | | | | | | | | | | |
| 1 | + | - | - | - | - | - | - | + | - | - | - | - | - | + | - | - | - |
| 2 | - | - | - | - | - | - | - | + | - | - | + | - | - | + | - | - | - |
| 3 | - | - | - | - | + | - | + | - | + | + | - | - | - | + | - | - | - |
| Yellow Cross | | | | | | | | | | | | | | | | | |
| 1 | ± | - | - | + | + | - | - | - | + | - | - | - | - | + | - | - | + |
| 2 | ± | - | - | + | + | - | - | - | + | - | + | - | - | + | - | - | + |
| 3 | - | - | - | - | - | - | - | - | + | - | + | - | - | + | - | - | + |
| 4 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | ak | + |

[a] Biochemical tests abbreviated as follows: ONPG=orthonitrophenol-galactopyranoside, ADH=arginine dihydrolase, CIT=citrate, URE=urea, VP=Voges-Proskauer, GEL=gelatin, MAN=mannitol, RHA=rhamnose, SAC=sucrose, ARA=arabinose, AMY=amygdalin, $NO_2$=nitrite, $N_2$=nitrogen, MOT=motility, MAC=MacConkey, OFO=glucose oxidation and CAT=catalase.

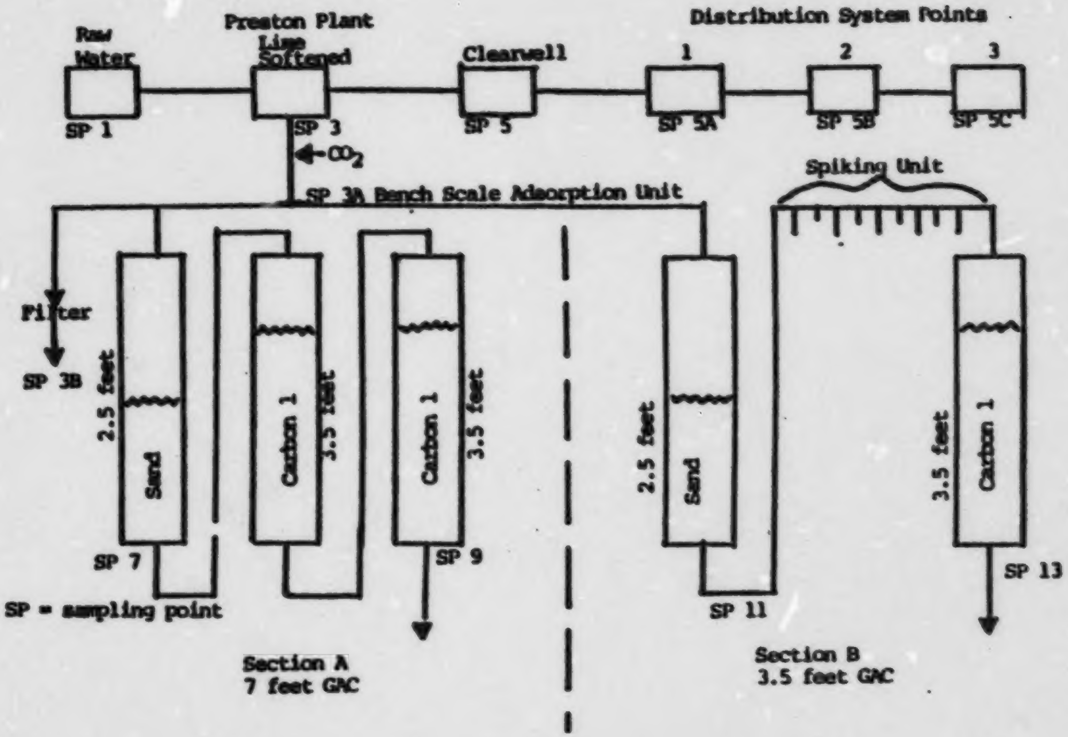

Raw Water
SP 1
Preston Plant
Lime Softened
SP 3
$CO_2$
Clearwell
SP 5
Distribution System Points
1
2
3
SP 5A
SP 5B
SP 5C
SP 3A Bench Scale Adsorption Unit
Spiking Unit
Filter
SP 3B
2.5 feet
Sand
Carbon 1
3.5 feet
Carbon 1
3.5 feet
SP 7
SP 9
SP = sampling point
Section A
7 feet GAC
2.5 feet
Sand
SP 11
3.5 feet
Carbon 1
SP 13
Section B
3.5 feet GAC

Figure 10 Flow Diagram for Evaluation of Carbon 1 on Lime-Softened Water

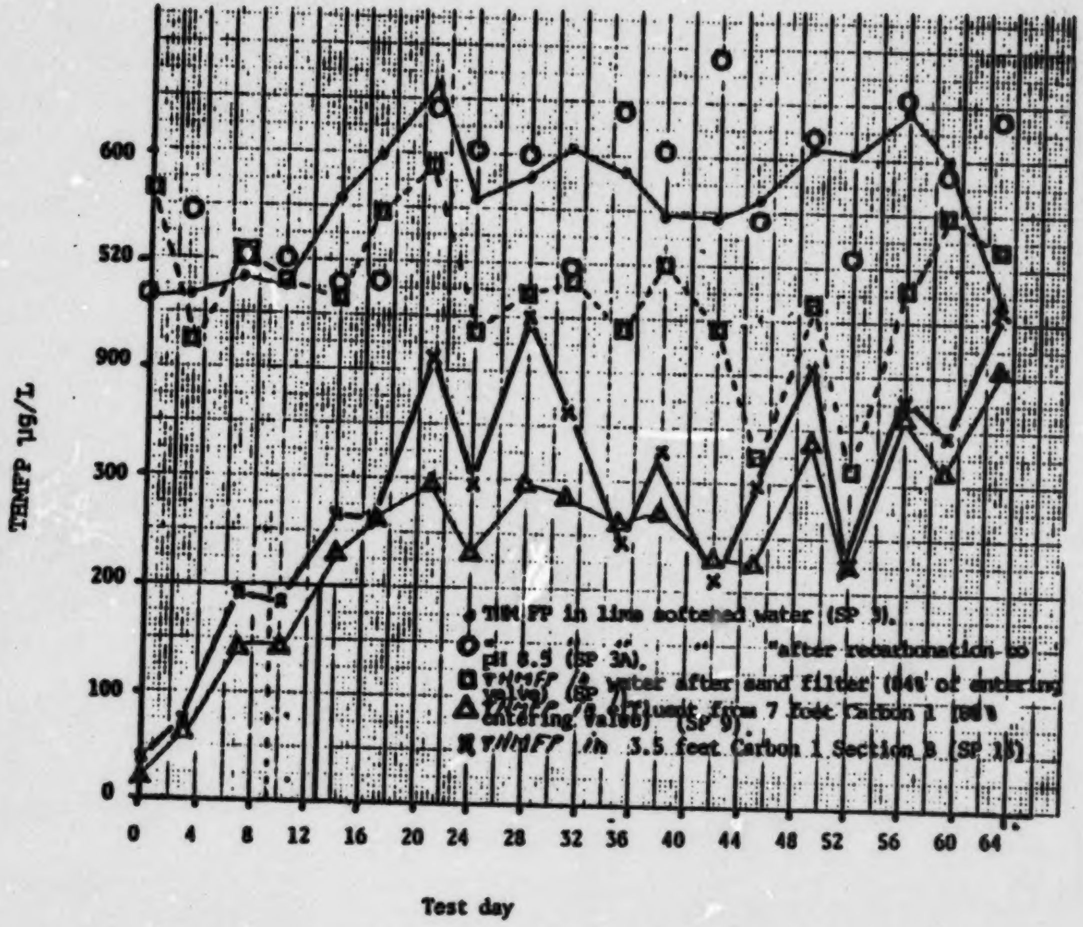


Figure 11 THMFP removal from Lime-Softened water by Carbon 1 in Section A

84 percent of the entering value. The average THMFP concentration from the sand column in Section B was 497µg/L, 88 percent of the entering value. Again, the analytical precision was good. The reduction of THMFP by the sand column could have been the result of removal of turbidity and its associated adsorbed coating of TOC (THMFP) substances, with an unknown contribution by the bacteria profile.

The THMFP breakthrough curve through the GAC column in Section A, Sampling Point 9, was plotted in Figure 11. Based on Criterion 1, breakthrough of 200 µg/L of THMFP, the bed life for 7 ft. of GAC on lime-softened water was approximately 13 days. THMFP breakthrough from 3.5 ft. of GAC from Section B, sampling point 13, was also plotted, with a bed life of approximately 7 to 9 days.

### A21112 TOC Removal by GAC in Section A of Bench-Scale Unit 1

TOC removal by 7 ft. of GAC in Section A was plotted in Figure 12. Sampling points plotted were Point 3, lime-softened water, Point 3A, after recarbonation, Point 7, effluent from sand filter column, and Point 9, effluent from the GAC column. The average TOC concentration in lime-softened water before and after recarbonation and after the sand column was 7.2, 6.9 and 6.6 mg/L, respectively. Based on Criterion 1, breakthrough of approximately 3 mg/L of TOC, the bed life of 7 ft. of GAC on lime-softened water was approximately 21 days.

### A21113 HOC Removal by GAC in Section A of Bench-Scale Unit 1

During the full 63 day test period, the average concentration of HOC in the raw, lime-softened and finished water at the Preston Plant is shown in Table 18. The average concentration in the effluent from the 2.5 ft. sand column is also shown.

The low levels of bromodichloromethane and chlorodibromomethane in the lime-softened water and in the sand column effluent waters was the result of the addition of silica activated with chlorine added to the lime-softeners in the Preston Plant as a flocculation aid. Breakpoint-chlorination in the Preston Plant increases the THM levels as shown. The finished water contained an average TTHM level of 162 µg/L.

HOC influent and effluent curves through the GAC column in Sections A and B for some of the compounds are plotted in Figure 13, 14 and 15. In Figure 13, chloroform level influent curves for the GAC columns are plotted as the concentration from the 2.5 ft. sand columns in both Sections A and B. Chloroform began to breakthrough 3.5 ft. of GAC, Section B, at test day 48. Saturation, influent equal to effluent, was probably reached by test day 63. The 7 feet GAC column in Section A showed no chloroform breakthrough at test day 63.

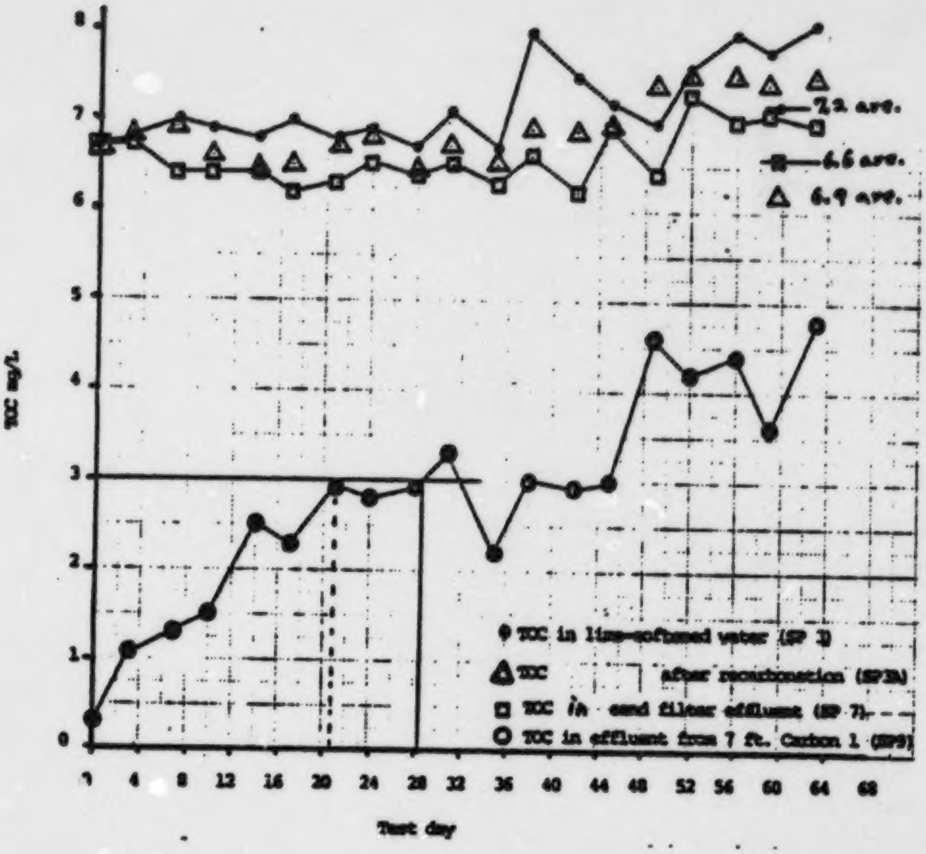


Figure 12 TOC removal from Lime-Softened water by Carbon 1 in Section A

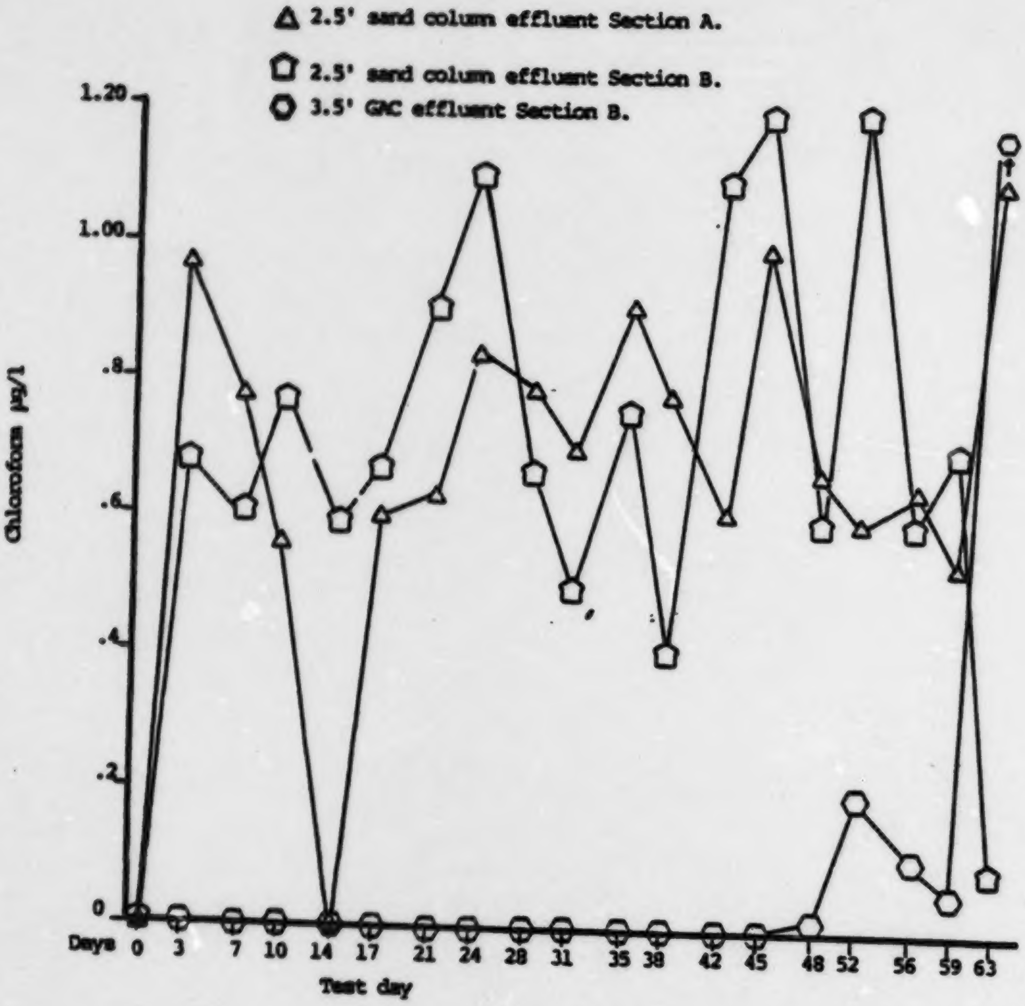


Figure 13 Chloroform in lime-softened effluent from sand and GAC columns

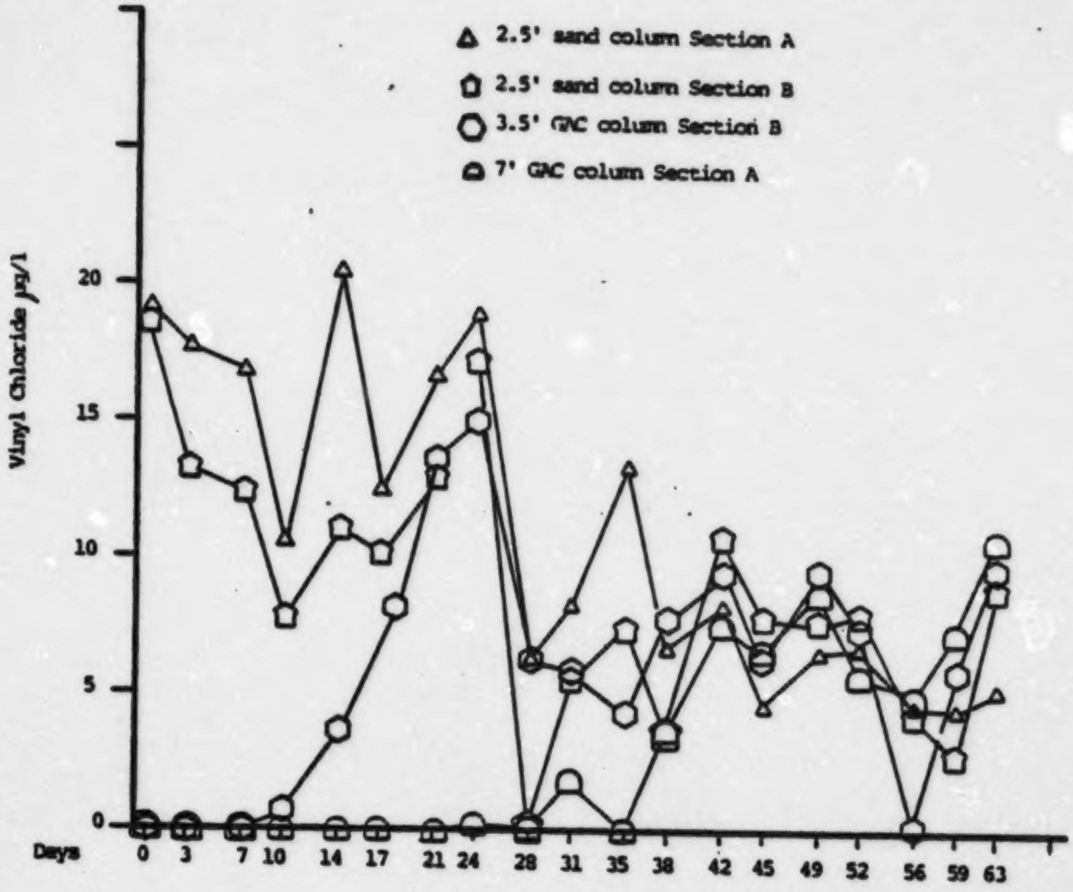


Figure 14 Vinyl chloride in lime-softened effluent from sand and GAC columns

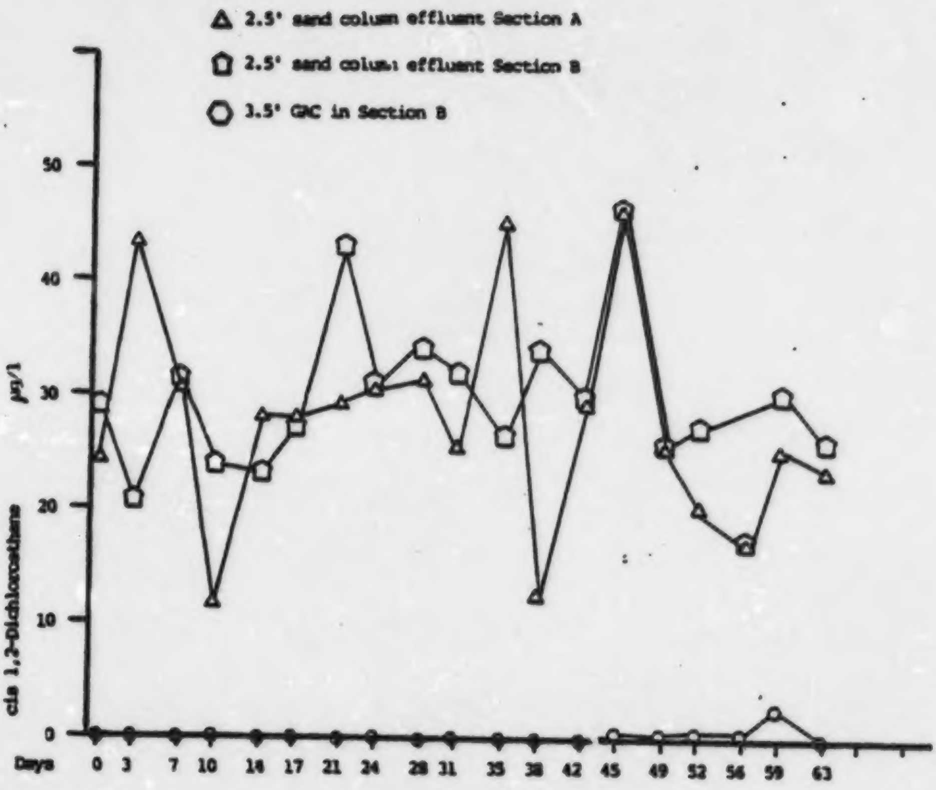


Figure 15 cis 1,2-Dichloroethene in lime-softened effluent from sand and GAC columns

## TABLE 18

## AVERAGE CONCENTRATION (μg/L) OF HOC DURING 63 DAY TEST PERIOD SECTION A, BENCH-SCALE UNIT 1

| HOC | Raw SP*#1 | Lime Softened SP #3 | Finished Water SP #5 | 2.5 Ft. Sand Column Effluent SP #7 |
|---|---|---|---|---|
| Vinyl chloride | 10.4 | 8.9 | 7.9 | 10.9 |
| Methylene chloride | 0.21 | 0.19 | 0.23 | 0.12 |
| trans 1,2-dichloroethene | 0.83 | 0.79 | 0.7 | 0.75 |
| 1,1-dichloroethane | 0.6 | 0.6 | 0.5 | 0.4 |
| cis 1,2-dichloroethene | 33 | 29 | 26 | 28 |
| Chloroform | 0.68 | 0.58 | 63 | 0.67 |
| Trichloroethylene | 0.56 | 0.47 | 0.47 | 0.54 |
| Bromodichloromethane | N | 0.19 | 55 | 0.22 |
| Chlorodibromethane | N | 0.03 | 38 | 0.06 |
| Chlorobenzene | 0.87 | 0.67 | 1.4 | 0.5 |
| Bromoform | N | N | 6 | N |
| p-chlorotoluene | 0.13 | 0.12 | 0.06 | 0.06 |
| p-dichlorobenzene | 0.51 | 0.44 | 0.37 | 0.34 |
| o-dichlorobenzene | 0.3 | 0.28 | 0.27 | 0.19 |

N = none detected
* SP = Sample Point Number

Vinyl chloride was plotted in Figure 14. Breakthrough and saturation for 3.5 ft. of GAC occurred at approximately 10 and 21 days, respectively. Breakthrough of cis 1,2-dichloroethene through 3.5 ft. of GAC in Section B, Figure 15, occurred at approximately test day 45. Breakthrough did not occur in the 7 feet GAC column in Section A. For the remaining HOC in Table 25, breakthrough did not occur during the full 63 day test period for either GAC column.

### A21114 Spiking Results from Section B of Bench-Scale Unit 1

Over a five year period of research on raw, lime-softened and finished water at the Preston Plant, we observed very few chemical pollutants above the molecular weight of the dichlorobenzene isomers. By liquid-liquid extraction, ECD, FID and GC/MS, very few peaks were found and the few found represented levels of less than 1 ppb. Because of this, we had no first hand way of observing the ability of GAC to remove pesticide or industrial organic pollutants from our high-TOC groundwater. If such pollutants ever enter our aquifer, it would be advantageous to know before hand the ability of GAC to remove them. Thus, in the bench scale research work, we began spiking such pollutants and observing their removal rate by GAC.

The results with six chlorinated pesticides are shown in Table 19.

## TABLE 19

## SPIKING LEVELS AND REMOVAL DATA ON SIX CHLORINATED PESTICIDES BY 3.5 FT. OF GAC (SECTION B)

| | μg/L Passed On TEST Day 0 | Ave. μg/L Influent/Day 28 Days | Ave. μg/L Passed/Day 28 Days | Ave. Percent Passed/Day 28 Days |
|---|---|---|---|---|
| γ BHC | 0.0000148 | 0.006 | 0.000102 | 1.7 |
| α BHC | 0.0000332 | 0.002 | 0.000058 | 2.9 |
| chlordane | 0.000072 | 0.004 | 0.00008 | 2 |
| Heptachlor Epoxide | 0.000829 | 0.016 | 0.00014 | 0.9 |
| dieldrin | 0.0000426 | 0.0007 | 0.00003 | 4.3 |
| oxychlordane | 0.000326 | 0.003 | 0.00009 | 2.9 |

The average concentration spiked in μg/L over the 28 day test period is shown in Table 26. The first effluent sample taken on day 0, was 30 minutes after the spiked water began flowing through the GAC column. At this 30 minute sampling point, all six chlorination pesticides were observed in the effluent at the concentration shown. The average concentration in the effluent over the full 28 day test period is shown, as well as the average percent passage.

Over a test period of 49 days, 2-nitrotuluene was spiked at an average concentration of 0.08 μg/L. This level was completely removed by the GAC up to test day 10. Breakthrough occurred, allowing up to 50 percent passage of the influent to test day 24. This was followed by a period, up to test day 38, of complete removal. This was followed by another period of breakthrough, averaging up to 5 percent of the influent, continuing to the end of the test period, 49 days.

Ethyl benzoate was spiked, average influent concentration 0.13 μg/L, for 49 days. Complete removal was achieved to test day 38. Breakthrough, up to 2 percent of the influent level, continued to the end of the test period. The spiking level of naphthalene over the 49 day test period was erratic, but averaged 0.3 μg/L. It was completely removed by the GAC.

The average influent concentration of 1-chloro-2- nitrobenzene was 0.05 μg/L. Except for low level breakthrough on test day 3, it was completely removed by the GAC to test day 38. Breakthrough, up to 10 percent of the influent level, occurred to the end of the 49 day test period.

Dimethylphthalate was spiked at an average concentration of 0.2 μg/L up to test day 10. It was completely removed by the GAC. After test day 10, varying amounts of this compound were observed in the blank, and it was necessary to abandon work on this compound.

Di-isobutylphthalate was spiked at an average concentration of 0.15 µg/L. Breakthrough, 16 percent of the influent level, occurred on test day 0. Low level passage was observed from test day 3 to 7, followed by 20 percent passage on test day 10. Passage increased, reaching the average influent level on test day 21. From test day 31 to the end of the 49 day test period, the GAC began to remove the compound once again, with passage averaging 3 percent of the influent level.

### A21115 Conclusions from Bench-Scale Unit 1

In previous research work, Ref. 6, with GAC Filtrasorb 400 (12 by 40 mesh, Calgon Corp., Pittsburg, Pa.) on finished water from the Preston Plant, it was found that when the effluent from a GAC column was rechlorinated to 3 mg/L of free chlorine and bottle-aged two days, it simulated the level of total trihalomethanes that could reach a consumer's tap. If a maximum level of trihalomehtanes of 100 µg/L is chosen, the bed lives of 2.5, 7.5, and 10 ft. of carbon were approximately 10, 65, and 81 days on finished water. The carbon use rate based on 10 ft. was 800 lb/mil gal. In this report, this basis for determining the effective GAC bed life on our water is referred to as "Criterion 1".

In this Pilot Plant research project, the following four commercially available carbons were selected for bench-scale study (on finished water) to select the best GAC for the Pilot Plant work.

| | |
|---|---|
| Carbon 1 | Filtrasorb 400, 12 by 40 mesh, Calgon Corp., Pittsburg, Pennsylvania |
| Carbon 2 | Nuchar WVG, 12 by 40 mesh, Westvaco Corp., Covington, Virginia |
| Carbon 3 Inc. | Hydrodarco 1030, 10 by 30 mesh, ICI Americas, Wilmington, Delaware |
| Carbon 4 Corp. | Witcarb grade 950, 12 by 30 mesh, Witco Chemical New York, New York |

The four types of GAC were evaluated in glass columns one inch in diameter. Equal volumes, 2.5 ft. of bed depth, were studied for a total test period of 59 days. Water flow rate was 3 gpm/ft$^2$ resulting in an EBCT of 6.2 minutes. As in the previous research work, Carbon 1, exhibited a bed life, based on Criterion 1, of 10 days for 2.5 ft. of GAC. The bed life for Carbons 2, 3, and 4 were less than 7 days, less than 3 days and approximately one day respectively. A comparison of the adsorption of each carbon at 10 days based on equal volumes and equal weight were as follows:

## TABLE 20
## PERCENTAGE OF INFLUENT THMFP ADSORBED BY EACH CARBON

| | Percentage Of Influent THMFP Adsorbed By Equal Volume | Percentage Of Influent THMFP Adsorbed By Equal Weights |
|---|---|---|
| Carbon 1 | 54 | 54 |
| Carbon 2 | 35 | 29 |
| Carbon 3 | 14 | 16 |
| Carbon 4 | 9 | 8 |

The removal of THMFP substances was the primary concern in this project. Carbon 1, Filtrasorb 400, was therefore selected as the best of the four studied.

TOC removal data at equal GAC volumes also showed Carbon 1, the best of the four. The previous research work showed that when the TOC breakthrough level reach approximately 3 mg/L, the GAC bed was exhausted, (Criterion 1). The four carbons in order, reached this effluent level in 10 days, 8 days, less than 4 days, and approximately 1-1/2 days. Removal capacity of HOC by GAC, while being important, was of less concern. However, over the full 59 day test period, the four carbons performed as follows based on chloroform removal:

## TABLE 21
## PERCENTAGE OF INFLUENT CHLOROFORM REMOVED BY EACH CARBON

| | Percentage Of Influent Chloroform Removed By Equal Volume Of GAC | Percentage Of Influent Chloroform Removed By Equal Weights Of GAC |
|---|---|---|
| Carbon 1 | 53 | 56 |
| Carbon 2 | 40 | 36 |
| Carbon 3 | 48 | 58 |
| Carbon 4 | 78 | 78 |

Carbon 4 showed the greatest adsorptive capacity for chlorform. Carbons 1 and 3 were similar, and Carbon 2 exhibited the lowest capacity. Similar ranking of the four carbons was observed with the removal of other HOC. However, Carbon 4 exhibited the least THMFP and TOC removal capacity.

Bed life exhaustion of 2.5 ft. of Carbon 1 at 10 days on finished water based on Criterion 1, was due almost entirely to THMFP breakthrough. If the THMFP substances were completely removed, bed life failure by TTHM breakthrough would have occurred at test day 35.

In the 59 day test of the four carbons on finished water, the average influent level of THMFP and TOC was 380 µg/L and 6.4 mg/L, respectively. The Pilot Plant project BAC towers would receive sand filtered lime-softened water recarbonated to a pH of 8.5. In another research phase of ED 1 using the same bench scale glass adsorption columns, 3.5 ft. and 7 ft. of Carbon 1 was tested on such a water feed. In the study the average influent level of THMFP and TOC was approximately 485 µg/L and 6.6 mg/L, respectively. The bed life for 3.5 and 7 ft. of Carbon 1, based on Criterion 1 (breakthrough of 200 µg/L of THMFP) was approximately 7 to 9 days, and 13 days, respectively. The bed life based on TOC removal, (breakthrough of approximately 3 mg/L of TOC) was 21 days for 7 ft.

Preliminary work on removal of spiked chlorinated pesticides and industrial chemical pollutants by Carbon 1, 3.5 ft. of bed depth, from our high TOC water source was begun in ED 1. Six chlorinated pesticides were spiked at average concentrations per day ranging from 0.0007 to 0.016 µg/L over a 28 day test period. At the first sampling time, 30 minutes after start of spiked water flow through the column, low level passage of all six pesticides, ranging from 0.0000148 to 0.000829 µg/L, was observed. Over the 28 day test period, the column allowed a percentage range of passage from 0.9 to 4.3 percent per day. The results with 5 industrial chemical pollutants was more variable.

## A212 Bacteriological Parameters

### A2121 Bench-Scale Unit 1 Results

Figure 16 is a flow diagram of the bench model used in this phase. The chlorination schedule is indicated with additional sampling points not shown in Section A, Figure 10. Total bacteria plate counts /mL obtained in ED 1, Phase 2 from unaged sand and GAC filter effluents are shown in Fig. 17. Raw water counts, not shown, ranged from zero to 300/mL with all except one count of less than 30/mL. Sand filter effluent counts ranged from 1200 to 71,000/mL. GAC unaged effluent counts ranged from 140 to 56,000/mL. Total plate counts/mL obtained from non-chlorinated samples, aged for up to ten days at room temperature to simulate distribution system residence time, are given in Table 22. Values obtained from aged treatment plant finished water are given for comparison.

After three days standing at room temperature, finished water and GAC effluent had counts of up to 1,000,000/mL with broad ranges of 0 to 1,000,000. Sand effluent had a lower maximum 300,000 after 3 days , and a narrower range, 100,000 - 300,000, of counts. After six days, counts from GAC effluents ranged up to 2,300,000/mL and the range had become wider 13,000 to 2,300,000. Apparently, the population size peaked by the tenth day when the maximum count of 2,300,000 fell to 360,000/mL, probably caused by depletion of nutrients or accumulation of toxic metabolites. Ranges given here necessarily are summations of the individual sample data. The increase followed by a decrease and sometimes another increase in counts/mL was often seen in water samples that were plated periodically and demon-

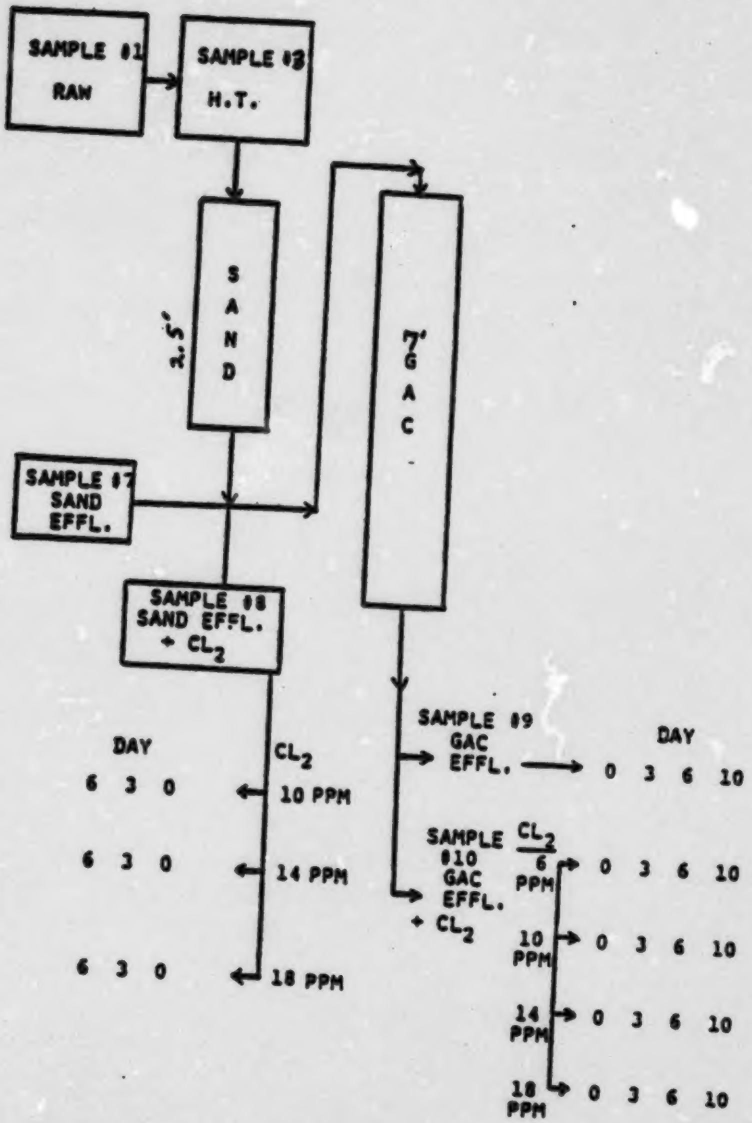

SAMPLE #1
RAW
SAMPLE #3
H.T.
SAND
2.5'
7'
GAC
SAMPLE #7
SAND
EFFL.
SAMPLE #8
SAND EFFL.
+ $CL_2$
DAY
$CL_2$
6 3 0
10 PPM
6 3 0
14 PPM
6 3 0
18 PPM
SAMPLE #9
GAC
EFFL.
DAY
0 3 6 10
SAMPLE #10
GAC
EFFL.
+ $CL_2$
$CL_2$
6 PPM
0 3 6 10
10 PPM
0 3 6 10
14 PPM
0 3 6 10
18 PPM
0 3 6 10

Figure 16 Sample points and sample treatment for bacteriological analyses.

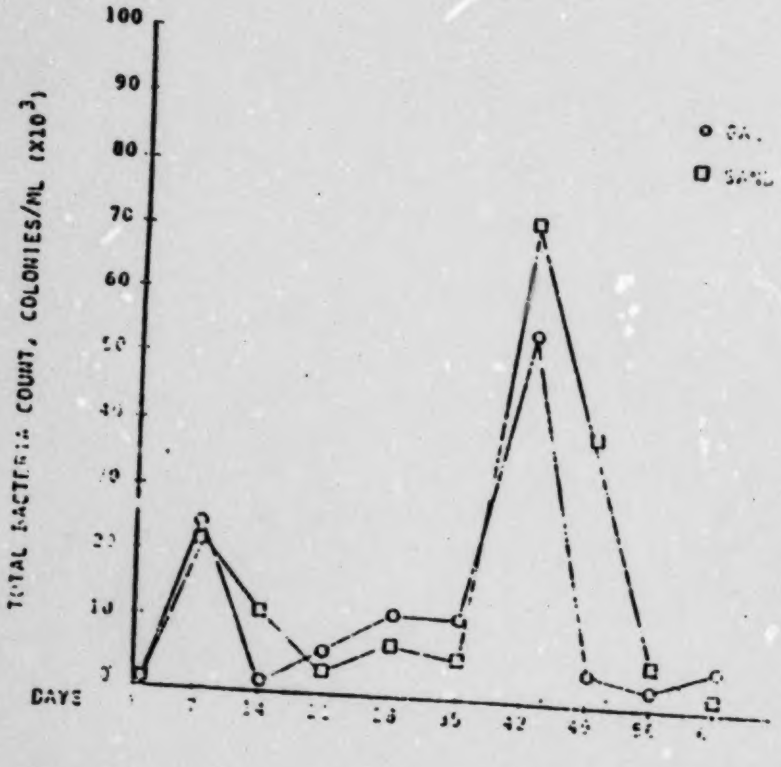


Figure 17 Total bacteria plate counts/mL obtained in ED 1, Phase 2 from unaged sand and GAC effluents.

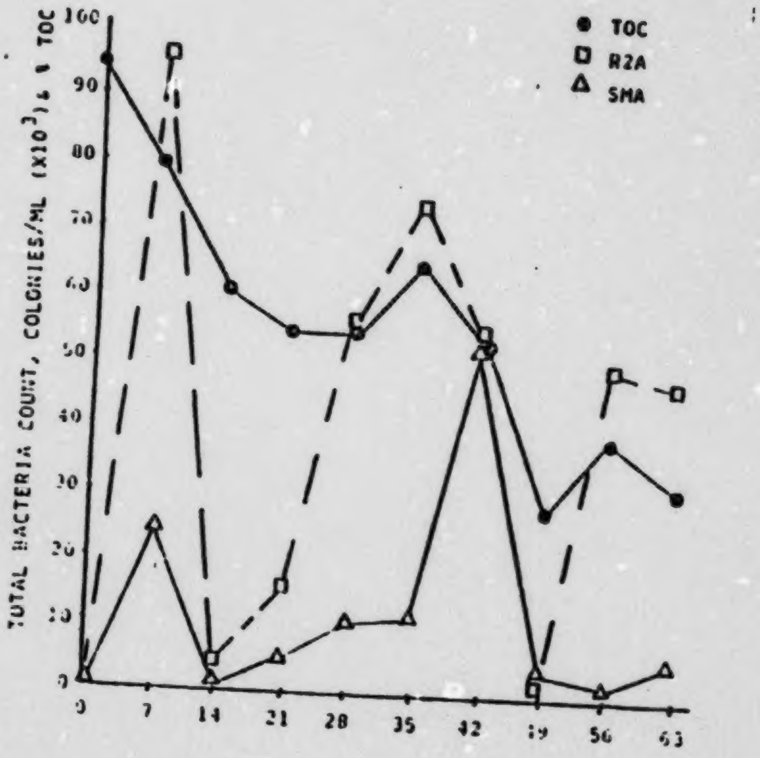


Figure 18 Bacteria plate counts/mL in GAC effluents and per cent TOC removed. Two media were used to increase probability of correlation.

strates species succession. A crude indication of this is seen in Table 23 where dominant organisms are listed with the percentage of possible times each was dominant during the aging of the samples.

The frequency of dominance; i.e., percent of the number of times the sample was plated that the organism was dominant, of each organism changed with the aging of the samples. Co-dominance of two or more organisms accounts for overlapping values (Table 23).

TABLE 22

RANGE OF BACTERIAL PLATE COUNTS/ML OBTAINED FROM NON-CHLORINATED AGED SAMPLES, AND TREATMENT PLANT FINISHED WATER, ED 1, PHASE 2

| AGE, DAYS | FINISHED WATER | SAMPLE<br>GAC EFFLUENT | SAND EFFLUENT |
|---|---|---|---|
| 0 | 0- 260* | 140- 56,000 | 1,200- 71,000 |
| 3 | 0- 1,000,000 | 37,000- 1,000,000 | 100,000- 300,000 |
| 6 | 20- 1,000,000 | 13,000- 2,300,000 | 12,000- 1,000,000 |
| 10 | 110- 1,000,000 | 38,000- 360,000 | ND |

*One count of 260 was obtained; all others were <10/mL

TABLE 23

OCCURRENCE OF DOMINANT ORGANISMS IN NON-CHLORINATED GAC EFFLUENTS, PERCENT OF TIMES POSSIBLE, ED 1, PHASE 2

| ORGANISM | AGE OF SAMPLE<br>0 DAYS | 3 DAYS | 6 DAYS |
|---|---|---|---|
| *Pseudomonas* spp. | 60* | 10 | 60 |
| Gram-positive rods | 50 | 20 | 30 |
| *Acinetobacter* spp. | 0 | 40 | 20 |
| *Moraxella* spp. | 30 | 10 | 20 |
| *Alcaligenes* spp. | 20 | 30 | 0 |
| Unidentified | 20 | 20 | 30 |

*Percentage

The frequency of dominance of organisms recovered from aged non-chlorinated sand filter effluents is shown in Table 24.

### TABLE 24
### OCCURRENCE OF DOMINANT ORGANISMS IN NON-CHLORINATED SAND FILTER EFFLUENTS, PERCENT OF TIMES POSSIBLE, ED 1, PHASE 2

| ORGANISM | AGE OF SAMPLE |  |  |
|---|---|---|---|
|  | 0 DAYS | 3 DAYS | 6 DAYS |
| Pseudomonas spp. | 40* | 66 | 66 |
| Gram-positive rods | 20 | 33 | 0 |
| Acinetobacter spp. | 40 | 0 | 0 |
| Moraxella spp. | 0 | 0 | 33 |
| Alcaligenes spp. | 0 | 66 | 0 |
| Unidentified | 10 | 0 | 0 |

*Percentage

Although the kinds of organisms recovered are the same as those found in GAC effluents, slight differences in the frequency of dominance of the different organisms can be seen. For example, in unaged GAC samples (0 Days, Table 23), Gram-positive rods and Pseudomonas spp. were most often dominant in the cultures made from them, but Pseudomonas spp. and Acinetobacter spp. were more frequently recovered as dominants from unaged sand filter effluent samples (Table 24). Acinetobacter spp. were not dominant in any unaged GAC effluent sample, although they were dominant 40 percent of the time in samples aged for three days. Pseudomonas spp. were most often dominant in both series of samples, and dominance alternated among the other species in both the GAC and sand effluent samples.

Survival of bacteria in chlorinated GAC effluents is shown in Table 25. The greatest count, 3,000 Gram-positive rods/mL, was obtained from three-days old effluent that had been chlorinated originally to 10 ppm, and had 0.56 ppm residual free chlorine at time of plating. Gram-positive rods were recovered from 27 of the 46 samples that yielded bacteria and were dominant in 20. Acinetobacter spp. occurred seven times and Pseudomonas maltophilia four times. Fifteen of the isolates were unidentified. Bacteria were recovered from 41 of the 121 samples of chlorinated GAC effluents that had residual chlorine at time of plating. An additional five samples yielded bacteria, but had no residual chlorine at time of plating.

Sand filter effluents yielded bacteria at all levels of chlorination as shown in Table 26; all were Gram-positive rods. Chlorine was effective in reducing bacteria counts/mL in both sand and GAC filter effluents to acceptable levels for acceptable periods of time by current standards. Survivors were most commonly Gram-positive rods, which were the only kind of bacteria recovered from sand effluents. Recovering the Gram-negative rods

## TABLE 25

## NUMBERS (TOTAL PLATE COUNT/mL) AND KINDS OF BACTERIA ISOLATED FROM CHLORINATED GAC EFFLUENTS AND PLANT FINISHED WATER

| No. Samples Yielding Growth (10 Sample Dates) | Original $Cl_2$ Conc. mg/L | Conc. $Cl_2$ At Plating | Count/mL (Range) | Dominant Organism |
|---|---|---|---|---|
| Aged 0 Days | | | | |
| 3 | 6 | 0.1 - 6 | 2 - 5 | G+ |
| 5 | 10 | 0.2 - 10.8 | 1 - 2 | G+ IV E |
| 2 | 14 | 6.4, 9.2 | 2, 15 | G+ |
| 2 | 18 | 6.2, 14.6 | 1 | G+/II F |
| Plant Fin. Water | 2 - 3 | 0.1 - 2 | 0 - 7 | G+ |
| Aged 3 Days | | | | |
| 1 | 6 | 4.6 | 12 | Unid. |
| 5 | 10 | 0.6 - 9.7 | 1 - 3000 | G+ |
| 4 | 14 | 2.9 - 8.2 | 1 - 3 | G+/Acinet.spp. |
| 1 | 18 | 6.2 | 4 | Acinet.spp. |
| Plant Fin. Water | 2 - 3 | 0 | $0 - 10^6$ | G+ |
| Aged 6 Days | | | | |
| 1 | 6 | 3.9 | 10 | P.maltophilia |
| 3 | 10 | 1.8 - 7.8 | 2 - 14 | Unid./ P.maltophilia |
| 3 | 14 | 5.2 - 10.9 | 2 - 30 | Unid. |
| 4 | 18 | 7.5 - 18.5 | 1 - 12 | G+/Unid. |
| Plant Fin. Water | 2 - 3 | 0 | $20 - 10^6$ | G+ |
| Aged 10 Days | | | | |
| 1 | 6 | 2.4 | 10 | G+ |
| 3 | 10 | 0.2 - 7.6 | 1 - 60 | Acinet.spp./G+ |
| 2 | 14 | 5.2, 10.4 | 1, 3 | G+ |
| 1 | 18 | 16.2 | 6 | G+ |
| Plant Fin. Water | 2 - 3 | 0 | $110 - 10^6$ | G+ |

*G+ - Gram-positive rods; IVE, IIF are CDC Groups; Acinet.=Acinetobacter spp.
Unid = Unidentified

such as CDC II F, CDC IV E, Pseudomonas maltophilia, Acinetobacter spp. and Unidentified spp. was the greatest single difference between chlorinated sand and GAC effluents. As these organisms have no special resistant form,

## TABLE 26

## BACTERIA (PLATE COUNT/mL)* RECOVERED FROM CHLORINATED SAND FILTER EFFLUENTS

| Sample Age, Days | Original Chlorine Level, mg/L | | | |
|---|---|---|---|---|
| | 0 | 10 | 14 | 18 |
| 0 | 2,000 - 23,000 | 2 | 14 | 0 |
| 3 | 100,000 - 300,000 | 3 | 0 | 0 |
| 6 | 12,000, 1,000,000 | 90 | 14 | 20 |
| $Cl_2$ at plating, mg/L | | 0.06 - 4.4 | 0.02 - 4.9 | 3.16 |

*Only Gram-positive rods were recovered from chlorinated sand filter effluents and only once during the experimental period from a sample at each chlorine level. The range of plate counts/mL for unchlorinated sand filter effluent is shown.

## TABLE 27

## BACTERIAL COLONY COUNTS/mL AND TOTAL ORGANIC CARBON REMOVED BY GRANULAR ACTIVATED CARBON FILTERS FROM LIME-SOFTENED UNCHLORINATED WATER

| DAY | Plate Count/mL | | TOC Removed* | |
|---|---|---|---|---|
| | R2A | SMA | mg/L | % |
| 0 | 220 | 140 | 6.4 | 95.5 |
| 7 | 95,000 | 25,000 | 5.1 | 79.7 |
| 14 | 4,400 | 1,000 | 3.9 | 60.9 |
| 21 | 16,000 | 5,200 | 3.4 | 54.0 |
| 28 | 55,000 | 11,000 | 3.5 | 54.7 |
| 35 | 74,000 | 12,000 | 4.1 | 65.1 |
| 42 | 52,000 | 56,000 | 3.3 | 53.2 |
| 49 | 100 | 4,200 | 1.8 | 28.1 |
| 56 | 50,000 | 1,900 | 2.6 | 37.1 |
| 63 | 48,000 | 5,000 | 2.2 | 31.4 |
| | | R2A | -0.21 | -0.19 |
| | | r = | | |
| | | SMA | -0.08 | -0.03 |

*Influent concentration minus effluent concentration.

most probably they survived inside cell aggregates that sloughed off colonies that grew too large to maintain their position on the GAC surfaces against the force of the flowing water. Apparently, sand did not allow this kind of growth. Although the same kinds of bacteria were present in both unchlorinated effluents (Tables 26 and 27), no Gram-negative rods were recovered from chlorinated sand effluent. Gram-positive rods, recovered from both sand and GAC effluents, probably survived chlorination as spores. No indicator organisms were recovered from any of the samples; none was present in the raw source water. The fact that Gram-negative rods, which have no special resistant form, were found in the presence of a free residual chlorine after several days aging of GAC effluents as shown in Table 25, may discourage the use of GAC as a final treatment step for polluted water. Enteric pathogens, which also have no special resistant form, may conceivably survive pretreatment and pass through GAC beds protected by the bacterial growth on the carbon. The pathogens may be unable to proliferate in the carbon beds, but may be included in the cell aggregates of soil bacteria found in GAC effluents. Thus pathogens may be able to survive further treatment of effluents as did the bacteria listed in Table 25.

A comparison of total organic carbon removed by GAC filters from influent lime-softened unchlorinated water with total bacteria plate counts/mL found in GAC column effluents is shown in Table 27 and Fig. 18. The sand filter removed no measurable TOC initially and thereafter removed from 0.1 mg/L to 1.0 mg/L, which was 1.5 percent to 13.5 percent, respectively, of the influent TOC concentration. The removal of the small and variable amounts of TOC by the sand was probably caused by straining out carbon-bearing lime particles mechanically carried from the Hydrotreator to the sand filter. Wood et al. (Ref. 1) reported that lime-softening and precipitation removed up to 30 percent TOC from raw water. No apparent agreement was shown between bacteria counts and amount of TOC removed. Correlations calculated by least squares between the bacteria counts/mL in the effluent and the amount of TOC removed were low and indicate little relationship existed. Figure 18 shows the bacteria counts/mL found in GAC effluents on SMA and R2A and the percent of TOC removed for the period of the experiment.

The percent of influent concentration TOC removed decreased with time as reported by Wood et al. (Ref. 1). The bacteria counts/mL increased and decreased from one sample time to another. Two media, SMA (Ref. 10) and R2A (Ref. 11), were used for plating to increase probability of demonstrating a correlation. Correlation coefficients for counts/mL on SMA vs amount and percent TOC removed are -0.08 and-0.03, respectively, on R2A medium they were -0.21 and -0.19, respectively.

## A22 Bench-Scale Unit 2

The preliminary spiking work in the preceeding section, Bench Scale Unit 1, resulted in design and operation of this study with some of the same chemicals, plus additional ones selected by EPA based on their current interests. The overall goals were:

1) the effectiveness of GAC and XE-340 resin to remove organic chemical pollutants from our high TOC finished water and,
2) development of methods of spiking such pollutants in bench scale testing.

### A221 Finished Water Source

Adsorbent columns were studied using two different finished water sources as influent. Study A used finished water from the clearwell piped directly to the water plant laboratory at the Preston Water Treatment Plant. Study B used finished water obtained from the water tap in our laboratory at Florida International University. This water originated at the Orr Water Treatment Plant in Miami, Florida. The organic composition of these two finished waters was different and they are described in detail later in this report.

### A222 Adsorbents Tested and Column Design

The two adsorbents used in both Studies A and B were as follows:

Filtrasorb 400, 12 X 40 mesh,
Calgon Corporation
Pittsburgh, Pennsylvania

Ambersorb XE-340
Rohm and Haas Company,
Philadelphia, Pennsylvania
A polymeric carbonaceous adsorbent
tailored for removal of low molecular
weight organics from water.

Both of the adsorbents above were from the same sample lots used in Ref. 1 and 2. The adsorbent column units in both identical, studies were as represented for Study A in Figure 19.

### A223 Water Flow Rates

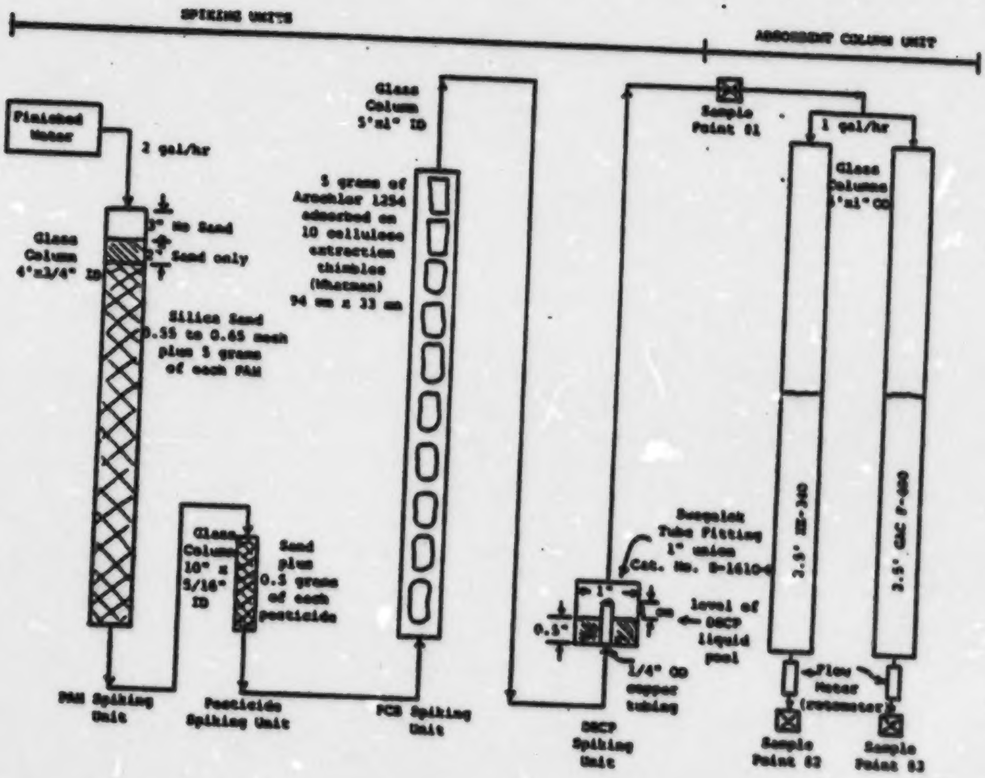

SPIKING UNITS
ADSORBENT COLUMN UNIT
Finished Water
2 gal/hr
3" No Sand
2" Sand only
Glass Column 4'x1/4" ID
Silica Sand 0.55 to 0.65 mesh plus 5 grams of each PAH
PAH Spiking Unit
Glass Column 10" x 5/16" ID
Sand plus 0.5 grams of each pesticide
Pesticide Spiking Unit
Glass Column 5'x1" ID
5 grams of Arochlor 1254 adsorbed on 10 cellulose extraction thimbles (Whatman) 94 mm x 33 mm
PCB Spiking Unit
Sample Point #1
1 gal/hr
Glass Columns 5'x1" OD
Swagelok Tube Fitting 1" union Cat. No. B-1610-6
1"
0.5"
level of DBCP liquid pool
1/4" OD copper tubing
DBCP Spiking Unit
3.5' XE-340
3.5' GAC F-400
Flow Meter (rotameter)
Sample Point #2
Sample Point #3

Figure 19 Spiking and Adsorption Unit at the Preston Plant (Study A)

The organic influent to the columns was measured at Sample Point 1 (Figure 19). The water flow at this point was two gallons per hour. This flow was then split to allow one gallon per hour through each adsorbent column. This or flow rate was regulated by a rotometer on the effluent end of each column. Each glass column, 5 ft. by one inch diameter, contained 2.5 ft. of adsorbent. This equal volume contained 176 grams of GAC and 215 grams of XE-340.

During the testing, there was no backwashing of the columns. As a result, the water pressure on the influent line had to be gradually increased to maintain the original one gallon per hour flow rate. When the pressure became too high, approximately 30 psi, we then lowered the flow rate to a given value, which lowered the influent pressure. When the pressure again became too high, the flow rate was again lowered. These different flow rates were used to calculate the influent and effluent concentration of each spiked compound. The flow rate changes are listed below in Table 28.

TABLE 28

WATER FLOW RATE THROUGH ADSORBENT COLUMN
(STUDIES A & B)

| Study A | | Study B | | Flow Rate (Gal/hr) |
|---|---|---|---|---|
| TEST DAY | DATE | TEST DAY | DATE | |
| 0 | 08/13/79 | 0 | 11/27/70 | 1 |
| 211 | 03/12/80 | 97 | 03/03/80 | 0.8 |
| 252 | 04/22/80 | 147 | 04/22/80 | 0.6 |
| 272 | 05/12/80 | 167 | 05/12/80 | 0.5 |
| 335 | 07/17/80 | 198 | 06/12/80 | 0.5 |

The initial flow rate of one gallon per hour through each adsorbent column was equal to a flow rate of 3 $gal/min/ft^2$, the flow rate through a rapid sand filter at the Preston and Orr Plants.

### A224 Spiking Procedures in Studies A and B

#### Study A

The flow diagram of the spiking units and the adsorbent columns for

Study A are shown in Figure 20. A separate spiking unit was used for PAH's, chlorinated pesticides, PCB and DBCP. Finished water, 2 gal/hr, flowed through the four spiking units arranged in series. This water flow was then split, allowing 1 gal/hr to flow through each adsorbent column.

1) PAH Spiking Unit

A glass column was used (4 ft. long and 3/4 inch I.D.) containing a glass frit on the bottom end to support the sand packing. Five grams of each PAH (crystals as received from supplier) were premixed with 0.55 to 0.65 mesh silica sand. This mixture was placed in the glass column. Two inches of pure sand were added to the top of the column. The water flowed down through the sand-PAH packing.

2) Chlorinated Pesticide Spiking Unit

A smaller glass column (10 inches long by 5/16 inch I.D.) with a glass frit on the bottom was used for this unit. The chlorinated pesticides (0.5 grams of crystals as received) were premixed with the sand. The water flowed down through the unit.

3) PCB Spiking Unit

Arochlor 1254 was the least water soluble chlorinated organic that was spiked. To achieve a significant spiking level, it was necessary to expose a very large surface area. The following system was devised. Five grams of Arochlor 1254 were dissolved in 70 mL of hexane. The bottoms were cut off the cellulose extraction thimbles (Whatman 94 mm X 33 mm). The resulting cylinders were cut up the side and formed into a loose spiral, the outer diamter was sized to fit into the one-inch I.D. glass column (five ft. long). Each cellulose spiral adsorbed one-tenth of the hexane-Arochlor solution. The spirals were air dried to remove the hexane and then placed in the glass column as shown in Figure 19. In this spiking unit, the water flowed upward.

4) DBCP Spiking Unit

This unit was designed to spike a rather high concentration. As shown in Figure 20, brass Swagelok tube fittings were used for the spiking device. DBCP, being heavier than water, formed a liquid reservoir in the bottom of the one-inch brass union (dimensions of the liquid reservoir are shown in Figure 20). The bottom of the brass spiking unit was a bore-through 1/4-inch Swagelok fitting. The water inlet 1/4-inch O.D. copper tube was extended one cm above the surface of the DBCP reservoir. The spiked water left the unit through a 1/4-inch fitting.

## Study B

In Study B, the PAH's were spiked exactly as shown in Figure 19 for Study A. The solid chlorinated pesticides and the PCB were not spiked in this study. DBCP was spiked at a much lower concentration. The DBCP spiking unit is shown in Figure 20.

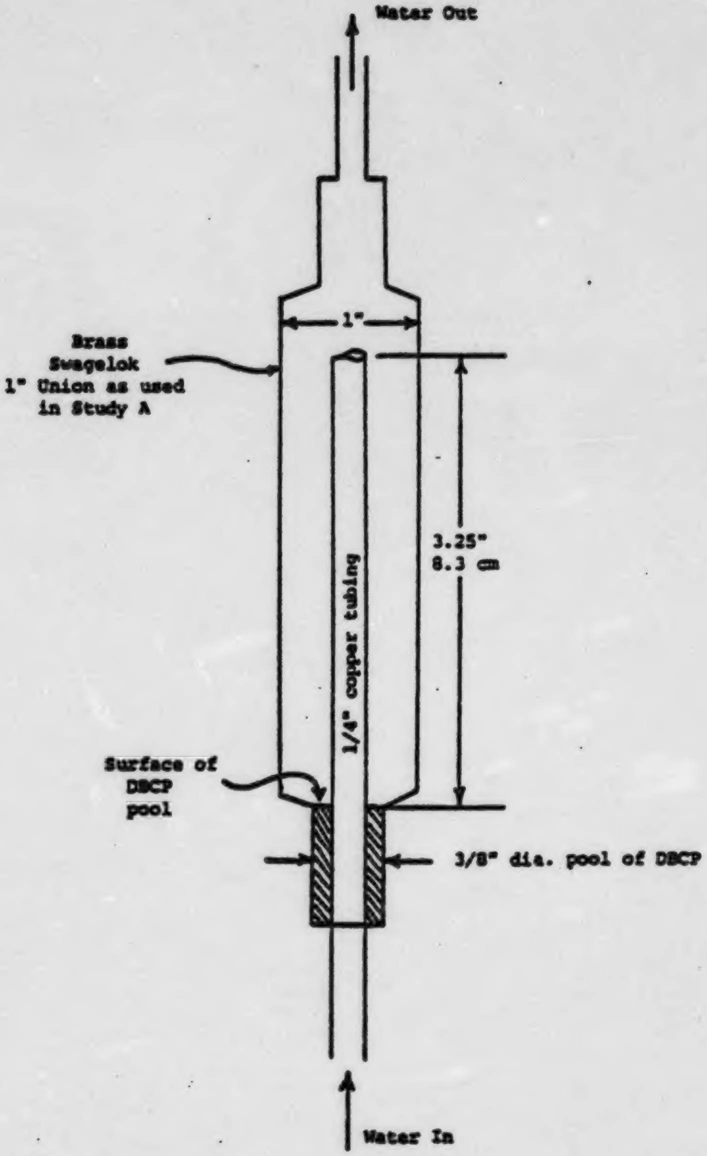

Water Out
1"
Brass Swagelok 1" Union as used in Study A
3.25" 8.3 cm
1/4" copper tubing
Surface of DBCP pool
3/8" dia. pool of DBCP
Water In

Figure 20 Dibromochloropropane Spiking Unit for Study B

Essentially, the lower spiked concentration was achieved by decreasing the exposed surface area of DBCP and lengthening the height of the 1/4-inch water inlet tube above the surface.

## A225 List of Spiked Organics

### Study A

Finished water at the Preston Plant was spiked with the following compounds.

PAH's -
naphthalene
acenaphthene
fluorene
anthracene
phenanthrene

pyrene

CHLORINATED PESTICIDES -
dibromochloropropane (DBCP)
hexachlorobenzene
γBHC
αBHC
pentachloronitrobenzene
aldrin
heptachlor

PCB -
Arochlor 1254

### Study B

Finished water from the Orr Plant was spiked with the PAH's above and DBCP.

## A226 Organic Loading on Adsorbent Columns from Finished Water

In our previous work, Ref.1, we showed that the naturally occurring organics in water (humic substances as measured by TOC) greatly affect the adsorptive capacity of a given adsorbent for a specific man-introduced pollutant, such as the volatile halogenated organics. We also showed that the adsorptive capacity for a specific halogenated organic was dependent on the concentration of other halogenated organics. Thus, to study the removal of spiked organics in this study, it was important to know the total organic loading on the adsorbent columns during spiking. Average influent concentrations of TOC, THMFP and HOC during the study period are shown in Table 29

## TABLE 29

## AVERAGE INFLUENT CONCENTRATION OF ORGANICS IN STUDIES A AND B

| | µg/L | |
|---|---|---|
| HOC | STUDY A | STUDY B |
| TOC | 7.2 mg/L | 5.0 mg/L |
| THMFP | 449 µg/L | 447 µg/L |
| vinyl chloride | 6.1 | nil |
| methylene chloride | 0.2 | 0.2 |
| trans 1,2-dichloroethene | 0.3 | 0.4 |
| 1,1-dichloroethane | 0.5 | nil |
| cis 1,2-dichloroethene | 25 | nil |
| chloroform | 112 | 155 |
| trichloroethylene | 0.3 | 0.4 |
| bromodichloromethane | 54 | 43 |
| tetrachloroethylene | nil | 0.04 |
| chlorodibromomethane | 37 | 16 |
| chlorobenzene | 1.6 | 0.9 |
| bromoform | 5 | 1.0 |
| p-chlorotoluene | 0.5 | nil |
| m-dichlorobenzene | nil | nil |
| p-dichlorobenzene | 0.2 | nil |
| o-dichlorobenzene | 0.2 | nil |
| TOTAL | 242.9 | 216.9 |
| TOTAL ETHENE COMPOUNDS | 31.7 | 0.8 |
| TOTAL TRIHALOMETHANES | 208 | 215 |

### A227 Discussion of Spiked Concentrations Achieved and Adsorption Results on Studies A and B

In the original report to EPA on this work, all experimental data were presented in three forms: 1) raw data tables of influent and effluent concentration (µg/L), 2) raw data graphs of influent and effluent concentration, and 3) a compiled table (Table 29) describing the average influent and effluent concentration per day in µg/L over specific time periods (taken from the graphed data); and also:

a. the total grams of each compound leached from each spiking unit,
b. the total grams of each compound entering each adsorbent column,
c. the total grams of each compound leaving each adsorbent column,
d. the precent of each compound leaving each adsorbent column based on the total grams entering.

To save space, the raw data tables are omitted here. Adsorptive performance for each compound follows:

1) PAH's

Naphthalene (in Table 30) was the most water soluble of the PAH's studied (33 mg/L). In both Studies A and B, before spiking units were connected to the adsorbent columns, finished water was allowed to flow through the spiking units for a time (approximately 1/2 hour), with the effluent going to collected waste. This was done to allow the spiking units to reach some degree of equilibrium before being connected to the adsorbent columns. In Study A, with naphthalene, this time was long enough, due to the relatively high solubility of this compound, to allow approximately 3.58 grams of the original 5 grams to pass from the spiking unit to collected waste. Thus, approximately 1.42 grams of naphthalene leached from the spiking unit during the entire Study A test period. One-half of the 1.42 grams entered each adsorbent column during the entire test period. Approximately one-half hour after initiating water flow through the spiking units, the effluent from the units was connected to the adsorbent columns. The concentration entering the columns from test day 0 to day 7 are shown in Figure 21. Influent and affluent concentrations in Study A for the full test period are plotted in Figure 21. A word description of the graphed influent data are given in Table 30, under the heading "average entering each column per day".

In Study B, the initial water flow time through the spiking units to reach some degree of equilibrium was shorter than in Study A. This was done to prevent the large loss to collected waste of the naphthalene experienced in Study A. Influent and effluent data are plotted in Figure 22. The influent concentration from day 0 through day 8 is also shown. The result, in Table 30, is that in Study B only one gram of the initial five grams of naphthalene went to collected waste. Four grams leached from the spiking unit during the entire Study B test period. Two grams of naphthalene thus entered each adsorbent column during the entire study period.

## Performance of Adsorbents on Naphthalene; GAC -

From Table 30, we observe that for naphthalene, the average concentration leaving the GAC columns in Study A was nil from test day 0 to test day 73, and in Study B was nil for 6 of the 11 sampling points to test day 45, with intermittent low pressage (averaging 0.023 μg/L) for the remaining 5 points. The loading of naphthalene was not constant, starting high, reducing steadily, and essentially all loaded on the columns after four weeks. The GAC column in Study B received 2.8 times

## TABLE 30. SPIKING AND ADSORPTION RESULTS ON GAC AND XE-340 ADSORBENTS (STUDIES A AND B)

| PAH Compound | M.W. | Solubility in Water | Grams Leached from Spiking Unit During Column, Tests |  | Grams Entering Each Column |  | Average Entering Each Column per Day |  | Average Leaving Each Column per Day |  | Total Leaving Each Column for Test Duration |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Study A | Study B | Study A | Study B | Study A µg/L | Study B µg/L | Study A (days) µg/L | Study B (days) µg/L | Study A grams | % | Study B grams | % |
|  |  | mg/L |  |  |  |  |  |  |  |  |  |  |  |  |
| Naphthalene | 128.17 | 33 | 1.42 | 4 | 0.71 | 2 | Start day 0 = 6200<br>Steady slope to day 9 = 20<br>Days 9 to 80 = 1<br>Day 80 to test end = small | Start day 0 = 17106<br>Steady slope to day 9 = 20<br>Steady slope to day 60 = 1.5<br>Day 61 to test end = 0.6 | XE-340<br>0 to 4=nil<br>4 to 17=0.36<br>17 to 46=5.0<br>46 to 129=10.2<br>129 to 221=11.2<br>221 to end=4.64<br>GAC<br>0 to 73=nil<br>80 to 108=0.136<br>108 to 207=nil<br>207 to end=0.0 | XE-340<br>0 =nil<br>1 to 52=1.3<br>52 to end=9.3<br>GAC<br>0 to 45= intermittent low passage 5 of 11 test points.<br>Average=0.02<br>52 to end=nil | XE-340<br>0.254929<br>GAC<br>0.00437 | 36<br>0.6 | XE-340<br>0.0003<br>GAC<br>nearly all removed | 4.4<br>~0 |
| Acenaphthene | 154.2 | 7 | 5 | 5 | 2.5 | 2.5 | Start day 0 = 1000<br>Steady slope to day 100 = 1.4<br>Day 100 to test end = 1.3 | Start day 0 = 1000<br>Steady slope to day 73 = 180<br>Day 101 to test end = 60 | XE-340<br>0 to 1=nil<br>3 to 52=0.56<br>52 to end=16.0<br>GAC<br>0 to end= 0 | XE-340<br>0 to 7=nil<br>7 to 87=5.52<br>87 to end=0.66<br>GAC<br>nil, 36 of 40 sample dates | XE-340<br>0.343275<br>GAC<br>nil | 13.7<br>~0 | XE-340<br>0.00003<br>GAC<br>~nil | 1.7<br>~0 |
| Fluorene | 166.2 | 1.9 | 5 | 5 | 2.5 | 2.5 | Start day 0 = 600<br>Steady slope to day 100 = ~0 | Start day 0 = 950<br>Steady slope to day 100 = ~0 | XE-340<br>0 to 45 cycle nil to 0.177<br>52 to end=2.64<br>GAC<br>0 to 73=nil (small)<br>73 to 115=0.34<br>115 to end=nil | XE-340<br>0 to 9=nil<br>9 to end=2.00<br>GAC<br>0 to 16=nil<br>23=0.12<br>23 to 67=nil<br>73 to 115=0.34<br>150 to end=nil | XE-340<br>0.05056<br>GAC<br>0.001175 | 2<br>0.05 | XE-340<br>0.02800<br>GAC<br>~nil | 1.1<br>~0 |
| Anthracene | 178.2 | .04 to .07 | 0.36 | 0.817 | 0.18 | 0.409 | Day 0 to 120=7.5<br>122 to end=2.7 | Day 0 to test end=28.4 | XE-340<br>0 to 14=nil<br>14 to end=0.2<br>GAC<br>0 to end=nil | XE-340<br>0 to end=nil<br>GAC<br>0 to end=nil | XE-340<br>0.004966<br>GAC<br>~nil | 2.0<br>~0 | XE-340<br>nil<br>GAC<br>~nil | 0<br>~0 |

(Cont.)

TABLE 30. (Cont.)

| PAH Compound | M.W. | Solubility in Water mg/L | Grams Leached from Spiking Unit During Column Tests |  | Grams Entering Each Column |  | Average Entering Each Column per Day |  | Average Leaving Each Column per Day |  | Total Leaving Each Column for Test Duration |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Study A | Study B | Study A | Study B | Study A µg/L | Study B µg/L | Study A (days) µg/L | Study B (days) µg/L | Study A grams | % | Study B grams | % |
| Phenanthrene | 178.23 | 1.10 to 1.29 | 5 | 5 | 2.5 | 2.5 | Start day 0 = 500<br>Steady slope to day 34 = 100<br>Steady slope to test end = 2 | Day 0 to 48=550<br>Steady slope to day 100 = 72<br>Steady slope to test end = 3.5 | XE-340<br>0 to 7=nil<br>9 to 46=0.5<br>50 to end=1.4<br>GAC<br>0 to end=nil | XE-340<br>0 to 1=nil<br>3 to 6=0.1<br>9 to 45=nil<br>52 to end=0.8<br>GAC<br>0 to end=nil | XE-340<br>0.139677<br>GAC<br>nil | 5.6<br>0 | XE-340<br>0.007763<br>GAC<br>nil | 0.3<br>0 |
| Fluoranthene | 202.26 | 0.21 to 0.26 | 4.5 | 2.694 | 2.25 | 1.347 | Day 0 to 115=10<br>115 to 179=56.<br>179 to end=5. | ← same | XE-340<br>0 to 17= nil<br>17 to 50=0.56<br>50 to 115=6.0<br>115 to end=2.3<br>GAC<br>0 to end= nil | XE-340<br>0 to 60=nil<br>60 to end=0.72<br>GAC<br>0 to end=nil | XE-340<br>0.143129<br>GAC<br>nil | 6.4<br>0 | XE-340<br>0.0129<br>GAC<br>nil | 1.0<br>0 |
| Pyrene | 202.26 | 0.132 to 0.13 | 1.076 | 1.425 | 0.537 | 0.713 | Day 0 to 80= 29.5<br>80 to end=15 | Day 0 to end= 49.5 | XE-340<br>0 to 17=nil<br>17 to 53=0.19<br>53 to 122=2.08<br>122 to end=0.422<br>GAC<br>0 to end=nil | XE-340<br>0 to 115=nil<br>150 to end=0.79<br>GAC<br>0 to end=nil | XE-340<br>0.018957<br>GAC<br>nil | 3.5<br>0 | XE-340<br>0.002257<br>GAC<br>nil | 0.3<br>0 |
|  |  |  | TOTAL | PAH's | 11.17 | 11.968 |  |  |  |  |  |  |  |  |
| Chlorinated Pesticides |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| DBCP | 236.3 | 1200 | 6.308 | 0.7684 | 3.154 | 0.3842 | Day 0 to 87=364<br>87 to end=17. | Day 0 to end= 26.7 | XE-340<br>0 to 7=nil<br>9 to end=25.4<br>GAC<br>0 to 28=nil<br>28 to end=8.5 | XE-340<br>0 to 52=0.005<br>52 to end=0.25<br>GAC<br>0 to end= 0.00116 | XE-340<br>0.584759<br>GAC<br>0.101152 | 10.5<br>5.7 | XE-340<br>0.062435<br>GAC<br>0.000017<br>(Cont.) | 0.6<br>0.004 |

TABLE 30. (Cont.)

| Chlorinated Pesticides (Cont.) | M.W. | Solubility in Water | Grams Leached from Spiking Unit During Column Tests | | Grams Entering Each Column | | Average Entering Each Column per Day | | Average Leaving Each Column per Day | | Total Leaving Each Column for Test Duration | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Study A | Study B | Study A | Study B | Study A µg/L | Study B µg/L | Study A (days) µg/L | Study B (days) µg/L | Study A (grams) | % | Study B (grams) | % |
| | | mg/L | | | | | | | | | | | | |
| Hexachloro-benzene | 285 | 0.11 | 0.0315 | | 0.0158* | | Day 0 to test end = 0.5 | | XE-340<br>0 to end=0.009<br>GAC<br>0 to end = 0.00075 | | XE-340<br>0.000225<br>GAC<br>0.000017 | 1.4<br>0.1 | | |
| αBHC | 291 | 7 | 0.00367 | | 0.00184* | | Day 0 to 4=0.74<br>4 to 35=0.08<br>35 to 196=0.045<br>196 to 229=0.246<br>229 to end=nil | | XE-340<br>0 to end = 0.001<br>GAC<br>0 to end = 0.000053 | | XE-340<br>0.000024<br>GAC<br>0.000001 | 1.3<br>0.05 | | |
| γBHC | 291 | 10 | 0.03 | | 0.015* | | Day 0 to end = 0.624 | | XE-340<br>0 to end = 0.032<br>GAC<br>0 to end = 0.0013 | | XE-340<br>0.000163<br>GAC<br>0.000032 | 1.1<br>0.2 | | |
| Pentachloro-nitrobenzene | 295.5 | 7 | 0.0726 | | 0.0363* | | Day 0 to end = 1.58 | | XE-340<br>0 to end = 0.133<br>GAC<br>0 to end = 0.0018 | | XE-340<br>0.003171<br>0.000043 | 0.7<br>0.1 | | |

(Cont.)

TABLE 30. (Cont.)

| Chlorinated Pesticides (Cont.) | M.W. | Solubility in Water | Grams Leached from Spiking Unit During Column Tests |  | Grams Entering Each Column |  | Average Entering Each Column per Day |  | Average Leaving Each Column per Day |  | Total Leaving Each Column for Test Duration |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Study A | Study B | Study A | Study B | Study A µg/L | Study B µg/L | Study A (days) µg/L | Study B (days) µg/L | Study A grams | % | Study B grams | % |
| Aldrin | 365 | mg/L<br>0.2 | 0.02167 |  | 0.0100* |  | Day 0 to 35 = 1.78<br>35 to end = 0.25 |  | XE-340<br>0 to end = 0.0352<br>GAC<br>0 to end = 0.0211 |  | XE-340<br>0.000814<br>GAC<br>0.000503 | 7.5<br>4.7 |  |  |
| Heptachlor | 373 | 0.056 | 0.144 |  | 0.072* |  | Day 0 to 22 = 2.8<br>22 to 207 = 0.61<br>207 to end = 0.18 |  | XE-340<br>0 to end = 0.071<br>GAC<br>0 to end = 0.00708 |  | XE-340<br>0.001693<br>GAC<br>0.000174 | 2.4<br>0.24 |  |  |
| TOTAL PESTICIDES *(-[illegible]PC) |  |  |  |  | 0.1517* |  |  |  |  |  |  |  |  |  |
| PCB |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Aroclor 1254 |  | 0.012 to 0.057 | 0.0793 |  | 0.0397 |  | Day 0 to end = 1.53 |  | XE-340<br>0 to end = 0.0093<br>GAC<br>0 to end = 0.041 |  | XE-340<br>0.00213<br>GAC<br>0.00098 | 5.4<br>2.5 |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

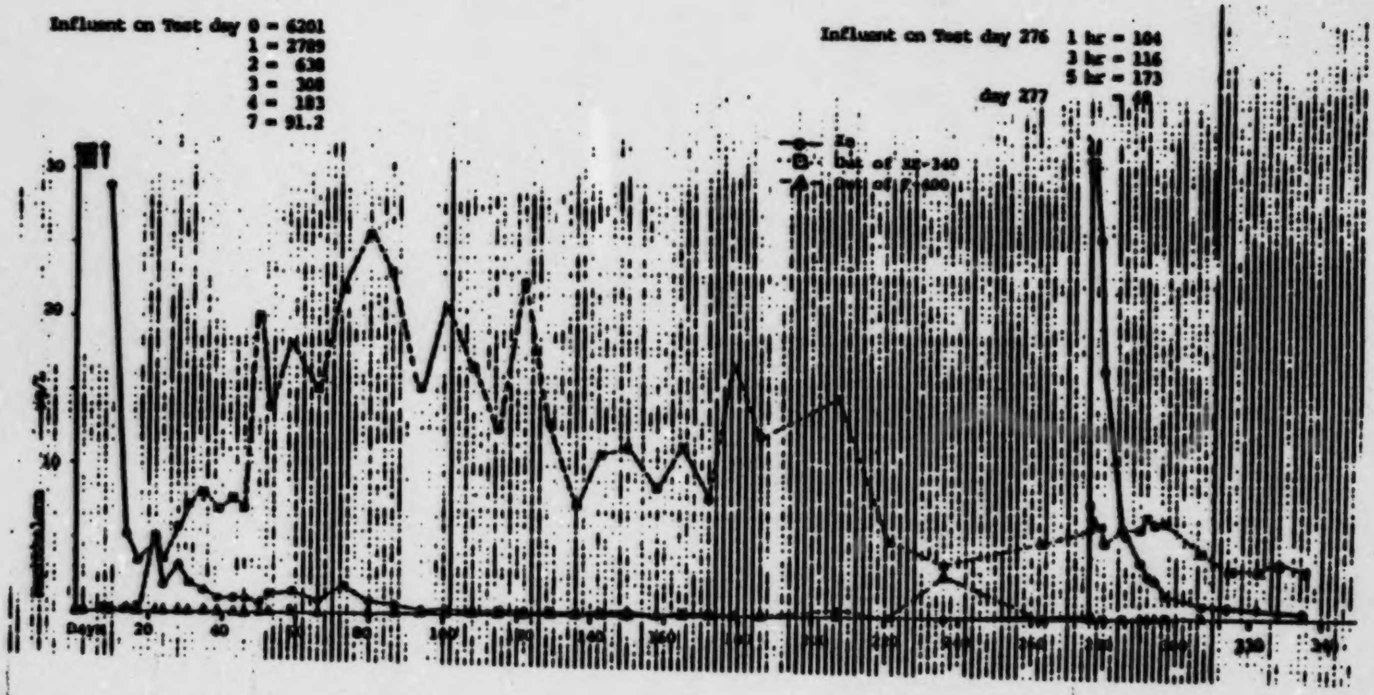


Figure 21 Naphthalene influent and effluents in Study A.

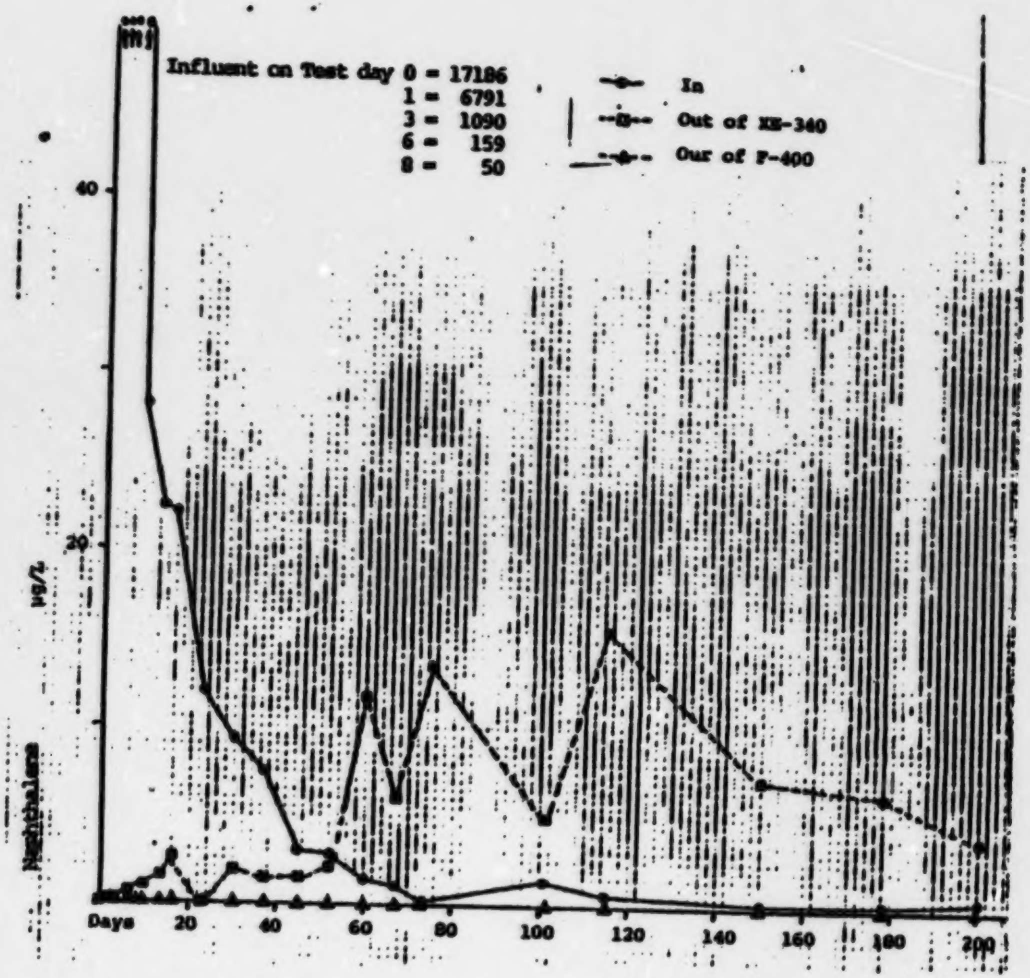


Figure 22 Naphthalene influent and effluents in Study B.

as much naphthalene as the column in Study A (2 grams vs. 0.71 grams). The columns in Studies A and B removed essentially 99.4 percent and 100 percent of the entering naphthalene, respectively (see last column of data in Table 30, "total leaving each column for test duration"). The column in Study B may have been more effective, despite the 2.8 times loading factor, because the competitive TOC loading factor, because the competitive TOC loading was less. In all cases throughout this spiking study, both adsorbents in Study B were more effective than in Study A. In Table 29, for each class of compounds spiked, the accumulated total grams entering each column in each study is shown. These values are helpful in visualizing overall organic loading on adsorptive results.

In Table 30, intermittent naphthalene breakthrough is shown on the GAC columns in both studies. In Study B, the intermittent low passage for the first 45 test days, followed by no passage at all to the end of the test period at day 198, indicates essentially no true breakthrough. In Study A, with intermittent breakthrough after test day 73, again it is doubtful that a true breakthrough state existed.

The discussion above on the adsorptive capacity of GAC F-400 for naphthalene of course applies only to our particular total organic loading water system. In addition, it pertains only to our particular sequence of organic loading on the virgin GAC. In Table 30, we observe that the GAC column in Study A actually adsorbed a total of 11.178 grams of PAH's, 0.15174 grams of chlorinated pesticides, and 0.0297 grams of PCB during the spiking test period. In addition, the unspiked organics were adsorbed. What would happen if at the end of the spiking test run, when the GAC had adsorbed its heavy loading of organics, we introduced another naphthalene spike? In Study A, after test day 73 the influent concentration of naphthalene average 0.2 µg/L per day to the end of the spiking test period, day 276. On test day 276, Study A, another small glass spiking column containing 10 mg of naphthalene dispersed in sand was put into the spiking system. The entire output was allowed to enter the XE-340 and GAC columns, thus each column received 5 mg. The concentration of naphthalene entering each column on test day 276, one, three and five hours after hooking up the new spiking unit, and on test day 277 is shown in Figure 21. The influent concentration for the remaining test period, to day 335, are plotted in Figure 21. In Figure 21, note that from test day 276, the first day of the second naphthalene spiking, to test day 335, no naphthalene was found in the GAC column effluent. Thus, even with the high organic loading on the GAC column, accumulated over 276 test days, a spike of 5 mg of naphthalene, producing a maximum concentration in the 173 µg/L range, was completely adsorbed and held for the remaining 59 days of the test period.

Spiking naphthalene data for GAC can be summed as follows:

1) In our particular organic loaded water system evaluated in this study, at a flow rate of 3 gal/min/ft$^2$, a virgin GAC (F-400) column 2.5 ft. deep essentially completely adsorbed two grams of naphthalene at an average loading of 2800 µg/L (high of 17,186 µg/L low of approximately 100 µg/L for the four days) over a four-day period. Continued water flow

through the column for approximately 276 days resulted in essentially nil displacement of the adsorbed naphthalene in the column effluent.

2) After 276 test days, the heavily organic loaded GAC column completelyadsorbed an additional 5 mg naphthalene spike and completely held the additional spike for the remaining 59 test days, to test day 335.

XE-340 -

From Table 30, we conclude that in both Studies A and B, the 2.5 ft. depth of XE-340 resin was probably right at or a little short of the mass transfer zone. In Study A, the XE-340 effluent data curve in Figure 21 follows the classic "S" shape adsorption isotherm curve, followed by a gradually decreasing curve, followed by a gradually decreasing curve representing displacement. While most of spiked naphthalene was adsorbed before test day 9, even at test day 276, the effluent average was approximately 10 μg/L. This slowly decreasing displacement would probably continue until most the initially adsorbed napthalene was removed. The maximum displacement concentration recorded (day 87) was 22.8 μg/L. At test day 276, the second spiked naphthalene loading was completely adsorbed and the remaining 59 test days still showed a decreasing concentration.

In Study B, (Figure 22) although the XE-340 column received 2.8 times the amount of naphthalene as Study A, it was all initially adsorbed. Breakthrough began after test day 1. The maximum effluent concentration (test day 115) was 15.52 μg/L. The sampling days were far apart at this critical time, so the maximum could have been higher. The maximum in the effluent, Figure 22 was followed by the typical gradually decreasing curve.

At the end of the test periods, the XE-340 columns in Studies A and B retained all but 36 percent and 4.4 percent of the entering napthalene, respectively. Once again, Study B, with less TOC loading than Study A, although receiving 2.8 times the level of napthalene, displayed the greatest overall removal. The XE-340 data on naphthalene can be summed as follows:

1) A loading of two grams of napthalene at an average loading rate of 2800 μg/L over a four-day period (high of 17,186 μg/L low of approximately 100 μg/L for the four days), was completely adsorbed for only one day. Initial breakthrough began at approximately one day. Continued water flow displaced the naphthalene in a typical "S" shaped adsorption isotherm curve. The maximum height of the curve was approximately 23 μg/L. The concentration in the effluent then steadily decreased, averaging approximately 5 μg/L at the end of the test, 335 days.

2) The XE-340 column on the lower TOC finished water source (5.0 vs. 7.2 mg/L) while receiving 2.8 times as much naphthalene loading (2 vs. 0.71 grams) displayed the greatest removal (95.6 percent vs. 64 percent) at the end of the testing periods.

3) The second naphthalene spiking (on test day 276) was essentially completely adsorbed by the XE-340 resin. For the remaining of the test period (59 additional days), breakthrough may have only increased from 5 to 6 µg/L.

## Acenaphthene

We do not have solubility data for this PAH, but in Table 29, we can conclude, comparing the naphthalene, acenaphthene and fluorene data, that the solubility probably falls between 1.9 and 33 mg/L. Approximately 2.5 grams of acenaphthene entered each adsorbent column in each study (Table 30). Influent and effluent data are plotted in Figures 23 and 24. The highest influent concentration was approximately 1000 µg/L in both studies. In Study A, most of the compound was loaded on the columns by day 108, averaging 1.3 µg/L loading from day 108 to the end of the test. In Study B, most of the compound was again loaded on the column by day 115, but the average for the remaining period was higher than in Study A, averaging 60 µg/L.

### GAC Results -

In both Studies A and B, the GAC columns, each loaded with 2.5 grams of acenaphthene, essentially completely adsorbed all the compound with no displacement over the entire test period.

### XE-340 Results -

From the data in Table 29, we conclude that the 2.5 feet of XE-340 resin allowed breakthrough of acenaphthene after 1 day in Study A, and after 7 days in Study B. The peak concentrations reached in the breakthrough curves were 9.7 µg/L on test day 28 for Study A and 40 µg/L on test day 150 for Study B. Breakthrough levels decreased from the peak levels reached to the end of the test period in both studies. However, even with some breakthrough, Studies A and B still showed that the XE-340 resin effectively removed 86.3 percent and 98.3 percent of the influent compound.

## Fluorene

Data are plotted in Figures 25 and 26. From Table 30, we observe that fluorene, with a solubility of 1.9 mg/L was completely leached from the PAH spiking unit in approximately 100 days in both studies. Thus, each column in each study received 2.5 grams of fluorene. From test day 100 on, the loading on the columns was essentially zero.

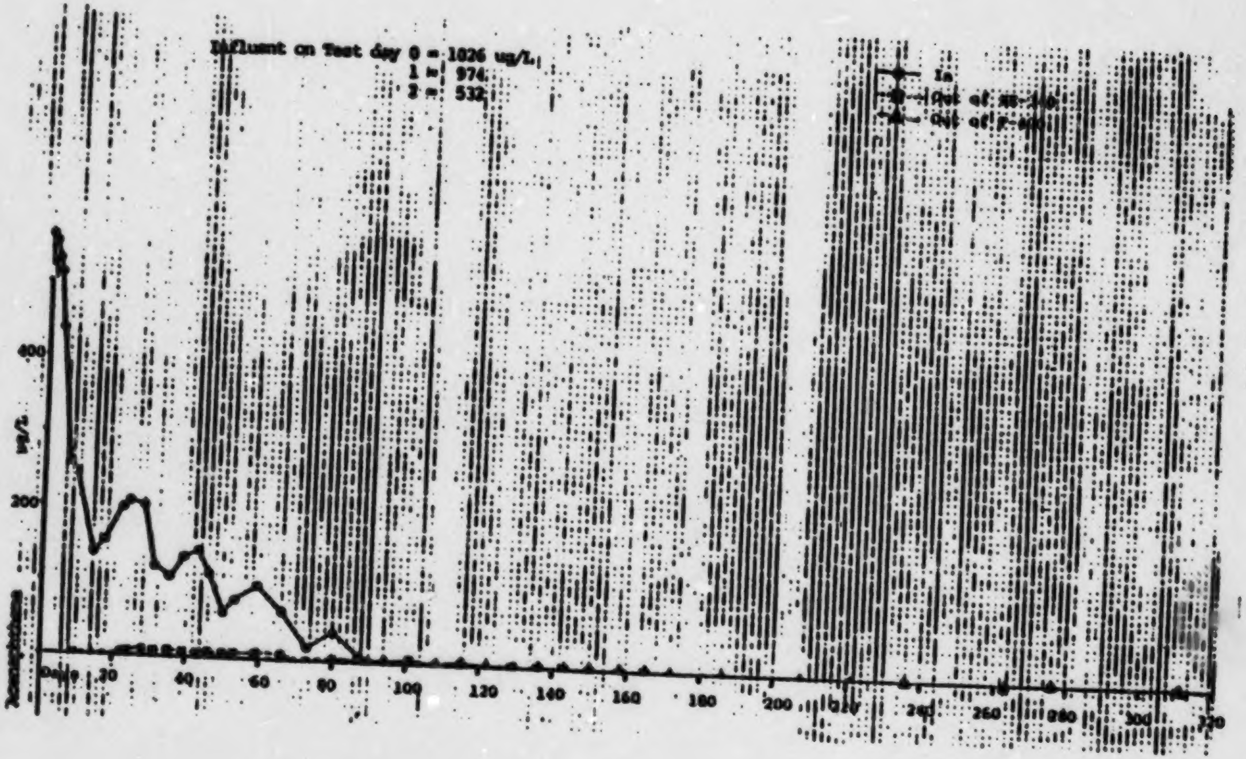


Figure 23 Acenaphthene influent and effluents in Study A.

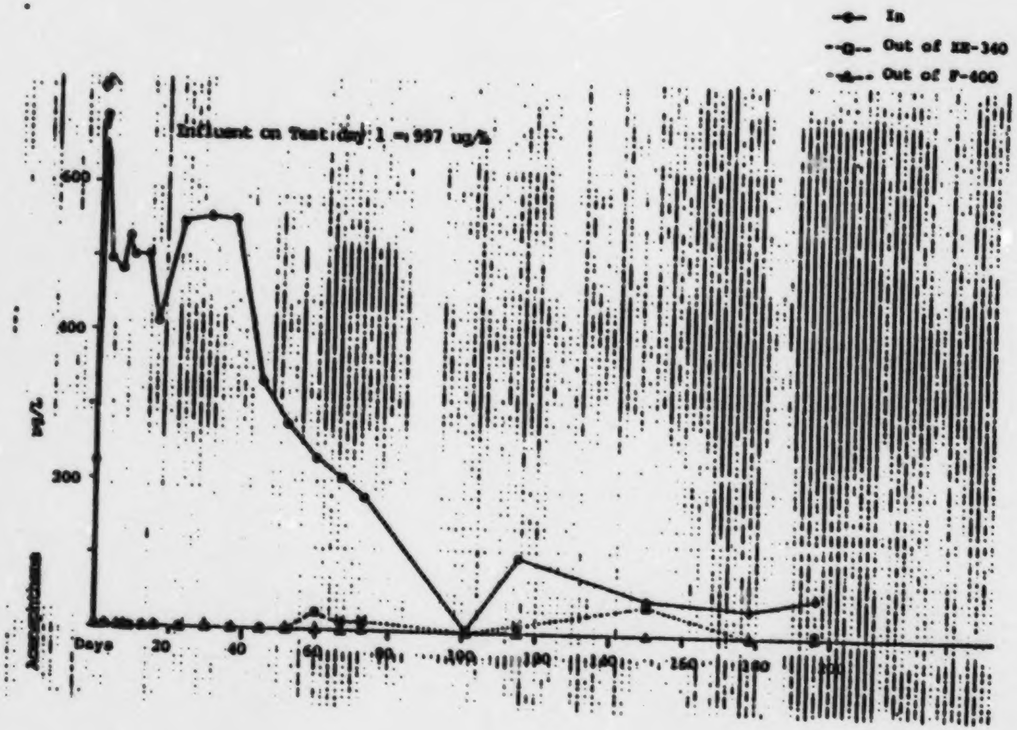


Figure 24 Acenapthene influent and effluents in Study B.

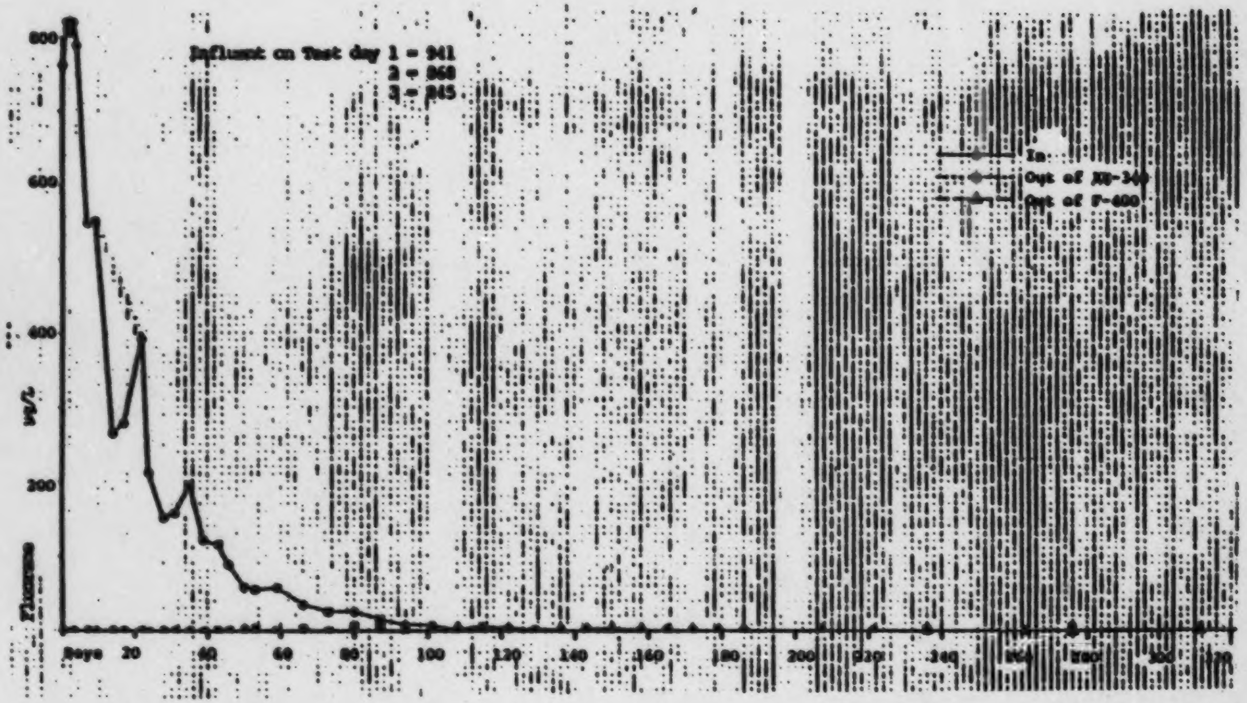


Figure 25 Fluorene influent and effluents in Study A.

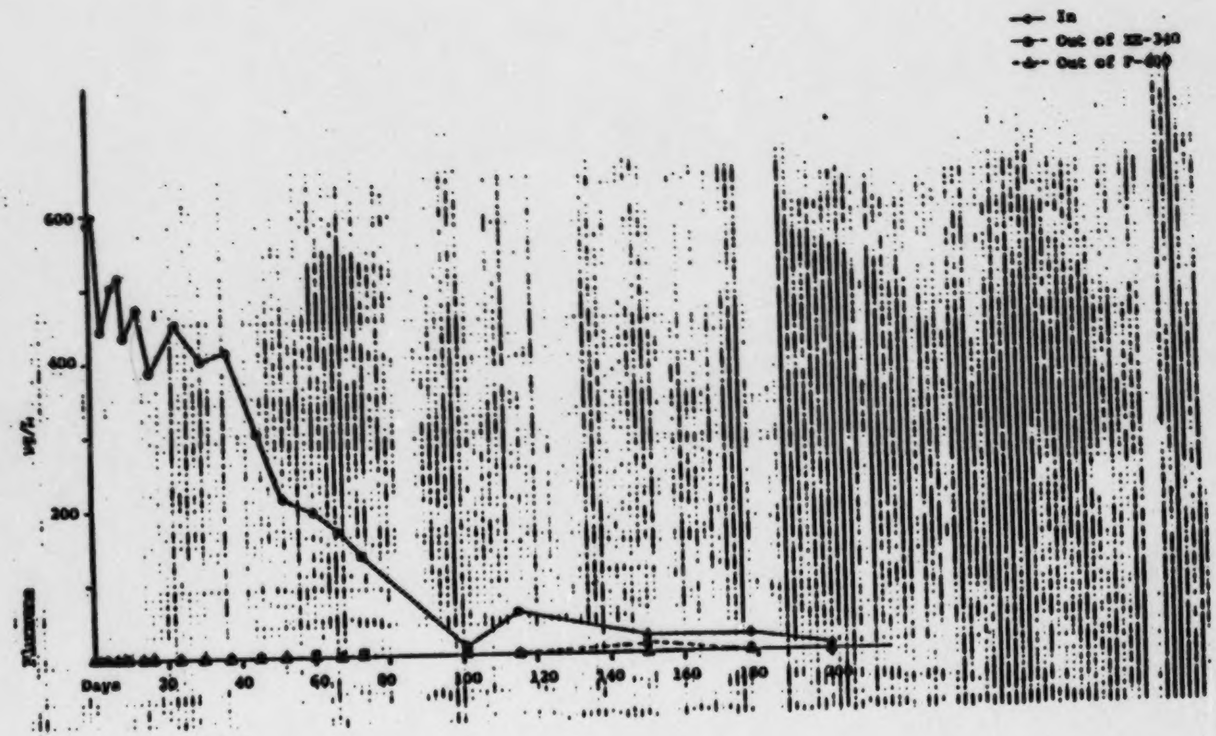


Figure 26 Fluorene influent and effluents in Study B.

GAC Results -

In both studies there was minor bleed from the columns (see Table 30 and Figures 25 and 26). In Study A and B, at the end of the tests, the GAC columns retained 99.95 percent and essentially 100 percent of the influent compound.

XE-340 Results -

There was less breakthrough than experienced for acenaphthene and naphthalene. At the end of the test periods, in Studies A and B, the XE-340 columns retained 98 percent and 98.9 percent of the compound.

## Anthracene

Because of the lower solubility of this compound, in Studies A and B, only 0.18 and 0.409 grams entered the adsorbent columns, respectively. Data are plotted in Figures 27 and 28.

GAC Results -

In both studies, throughout the test periods, there was essentially no anthracene in the GAC column effluents. Adsorption was essentially 100 percent.

XE-340 -

In Study A, some breakthrough was observed, resulting in 97.2 percent adsorption at the end of the test. In Study B, removal was 100 percent.

## Phenanthrene

Solubility of this compound was close to the solubility of fluorene, and we again observed that each column in each study received 2.5 grams of the compound. Data are plotted in Figure 29 and 30.

GAC Results -

In both studies, GAC removed 100 percent for the entire test periods.

XE-340 -

In Study A, breakthrough resulted in 94.4 percent removal. Removal in Study B was 99.7 percent.

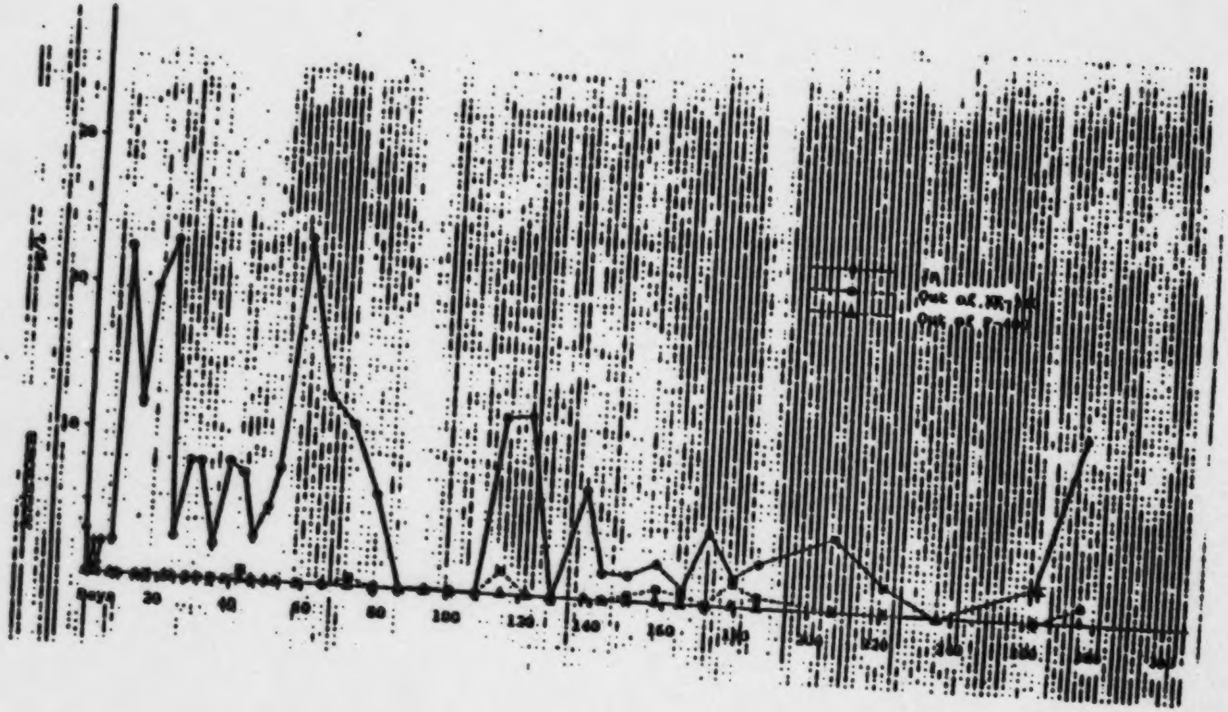


Figure 27 Anthracena influent and effluents in Study A.

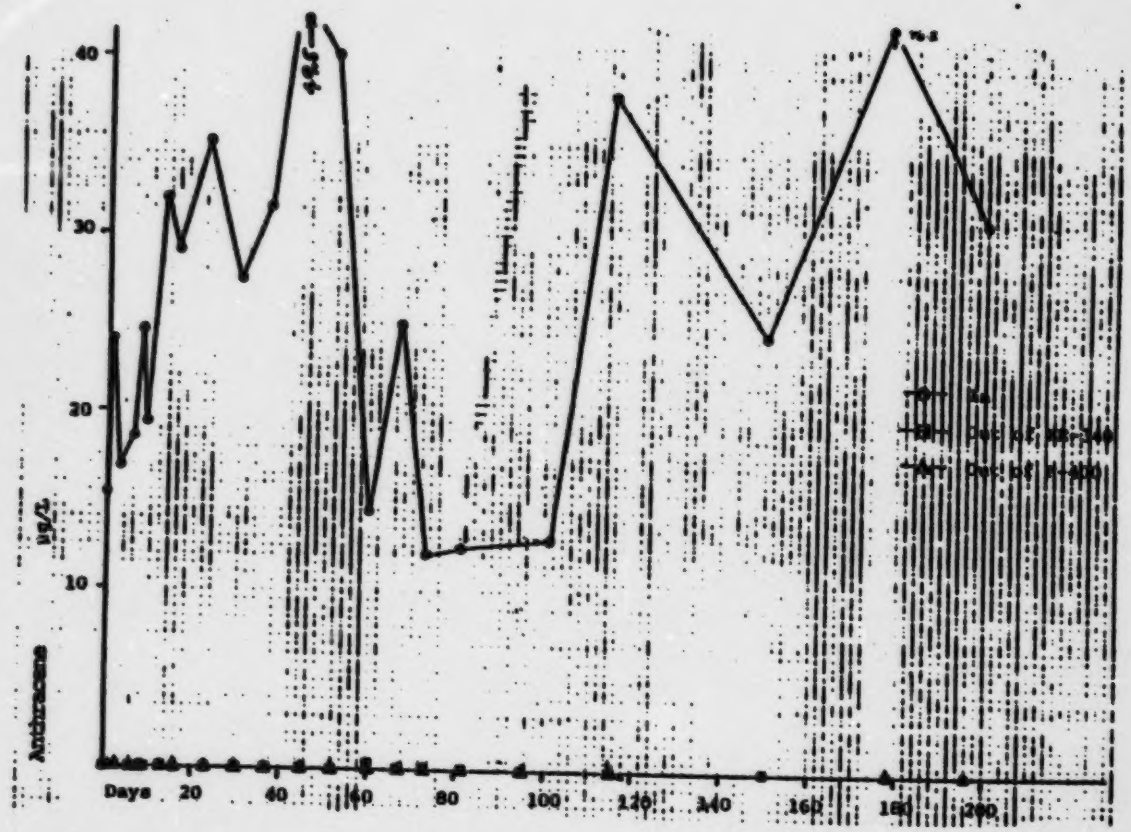


Figure 28  Anthracene influent and effluents in Study B.

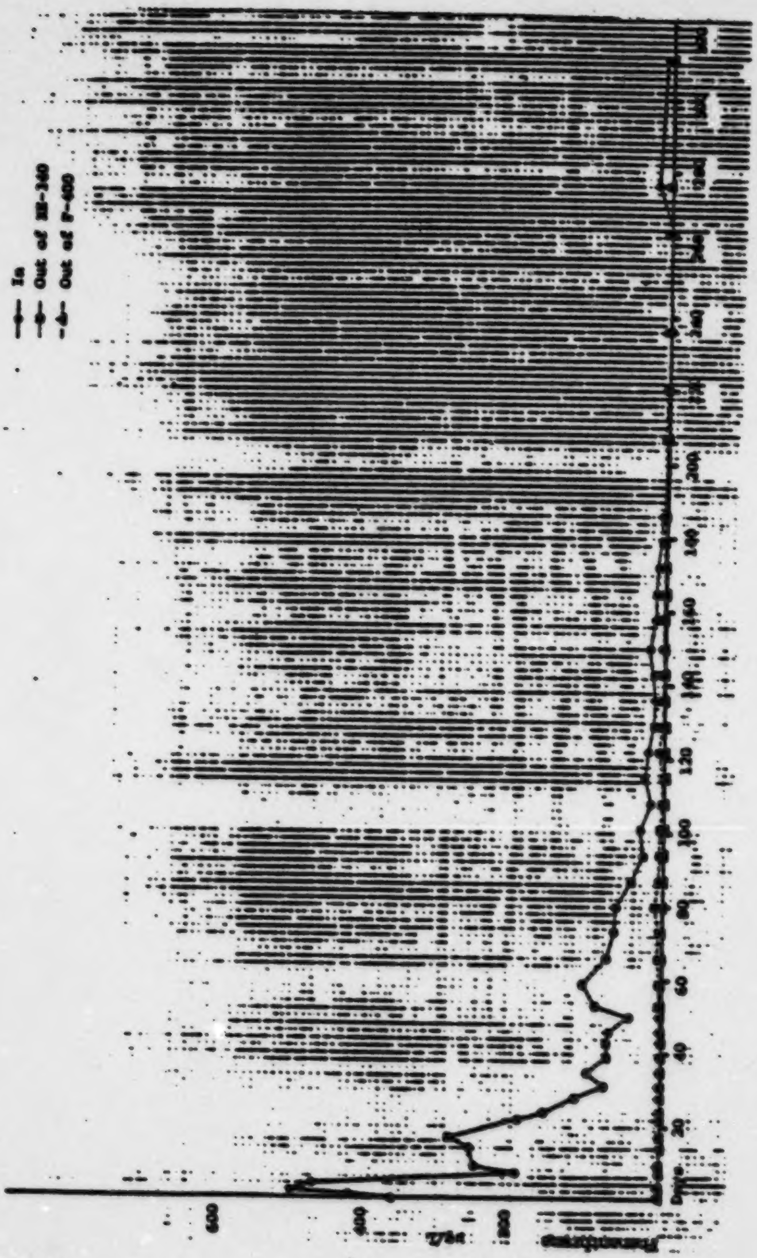


Figure 29 Phenanthrene influent and effluents in Study A.

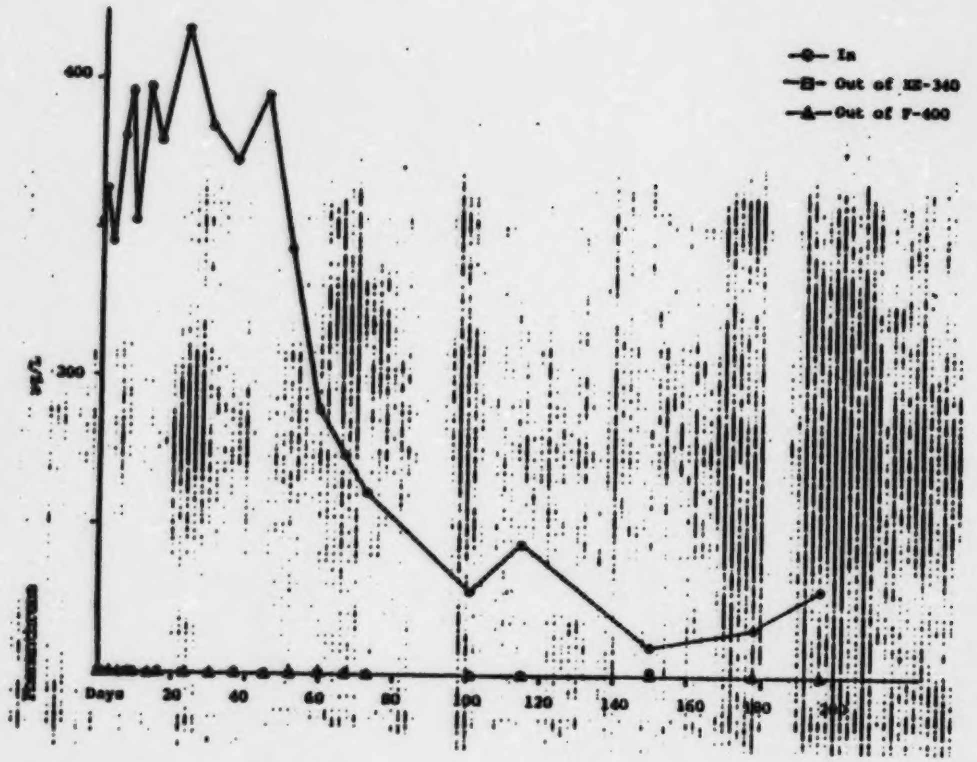


Figure 30 Phenanthrene influent and effluents in Study B.

### Fluoranthene

Throughout the test periods, 2.25 and 1.347 grams entered each column in Studies A and B, respectively. Data are plotted in Figure 31 and 32.

GAC Results -

In both studies, GAC again removed 100 percent for the entire test periods.

XE-340 -

Breakthrough resulted in 93.6 percent removal in Study A, and 99 percent removal in Study B.

### Pyrene

In Study A, 0.537 grams entered each column, while in Study B, 0.713 grams entered each column. Data are plotted in Figure 33 and 34.

GAC Results -
GAC resulted in 100 percent removal in both studies.

XE-340 -

Breakthrough resulted in 96.5 percent removal in Study A, and 99.7 percent in Study B.

## 2) Chlorinated Pesticides

### DBCP

Dibromochloropropane (DBCP) was just beginning to appear in some wells in California at the start of this spiking study. EPA, therefore, wanted this substance included. In Study A, a DBCP spiking unit was devised, hoping for a spiking concentration of approximately 10 to 25 µg/L. Instead, as shown in Table 30, a much higher spiking level was obtained, 364 µg/L average from day 0 to day 87, and 17.9 µg/L from day 87 to the end of the test. Study B was started, hoping to achieve the desired spiking level by building a new DBCP spiking unit. As shown in Table 30, it was quite successful, averaging 26.7 µg/L over the entire test period.

DBCP being quite water soluble (1200 mg/L), should be adsorbed more in line with the adsorptive properties of the volatile halogenated organic studied in Ref. 1. Refer to Table 30 and Figures 35 and 36 for test data details.

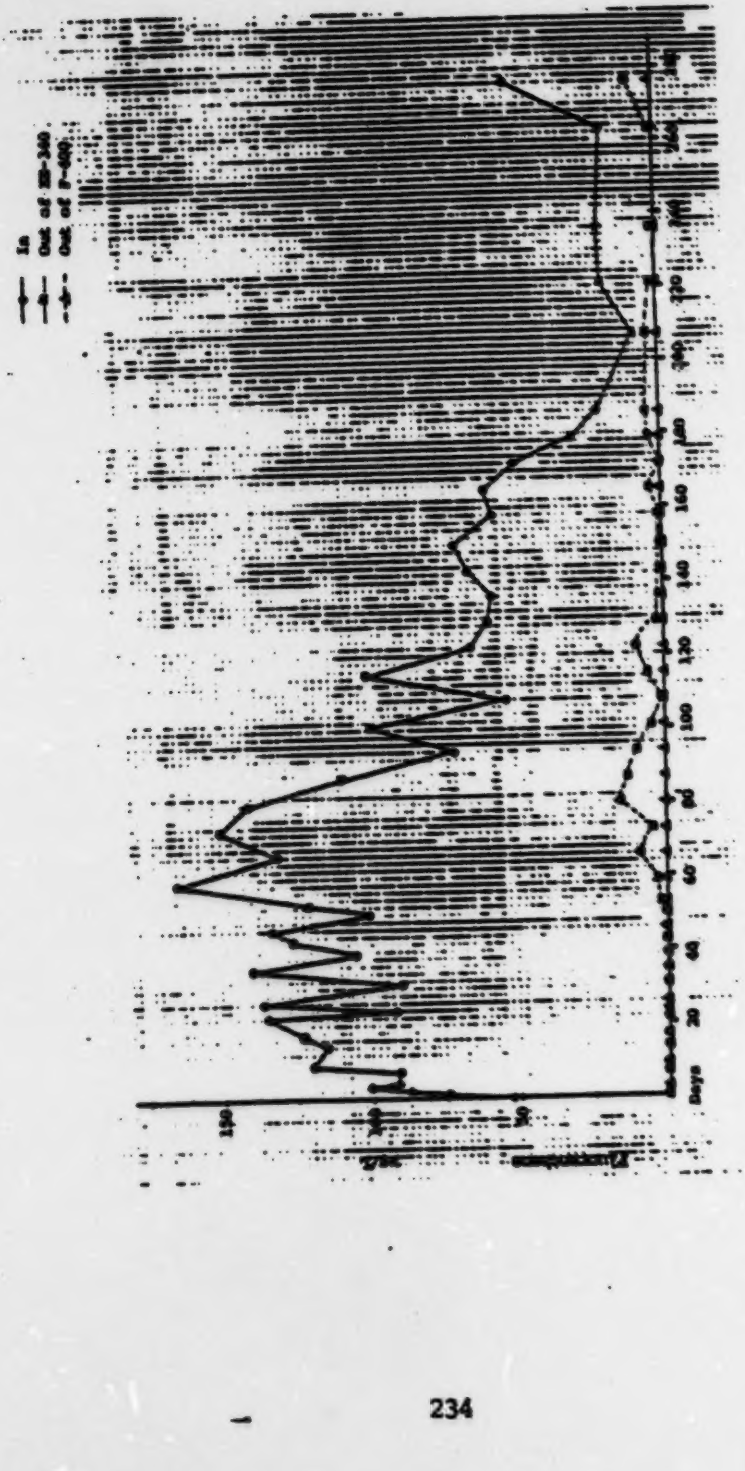


Figure 31 Fluoranthene influent and effluents in Study A.

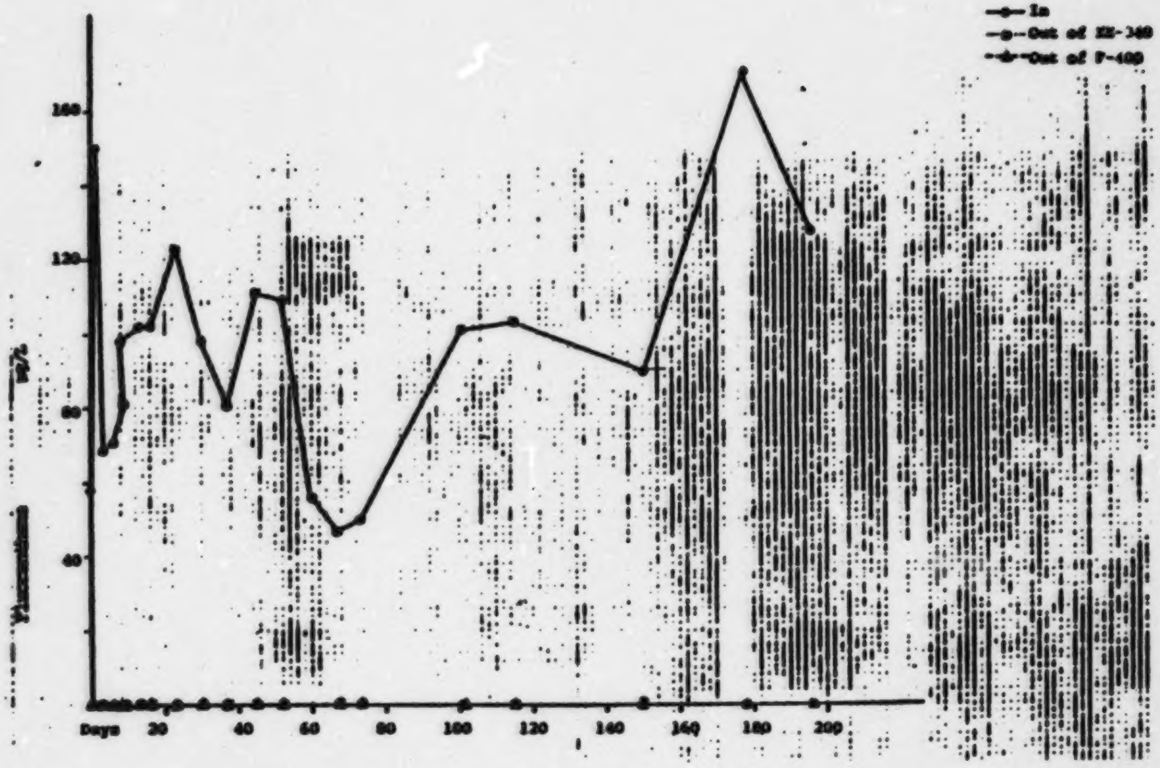


Figure 32 Fluoranthene influent and effluents in Study B.

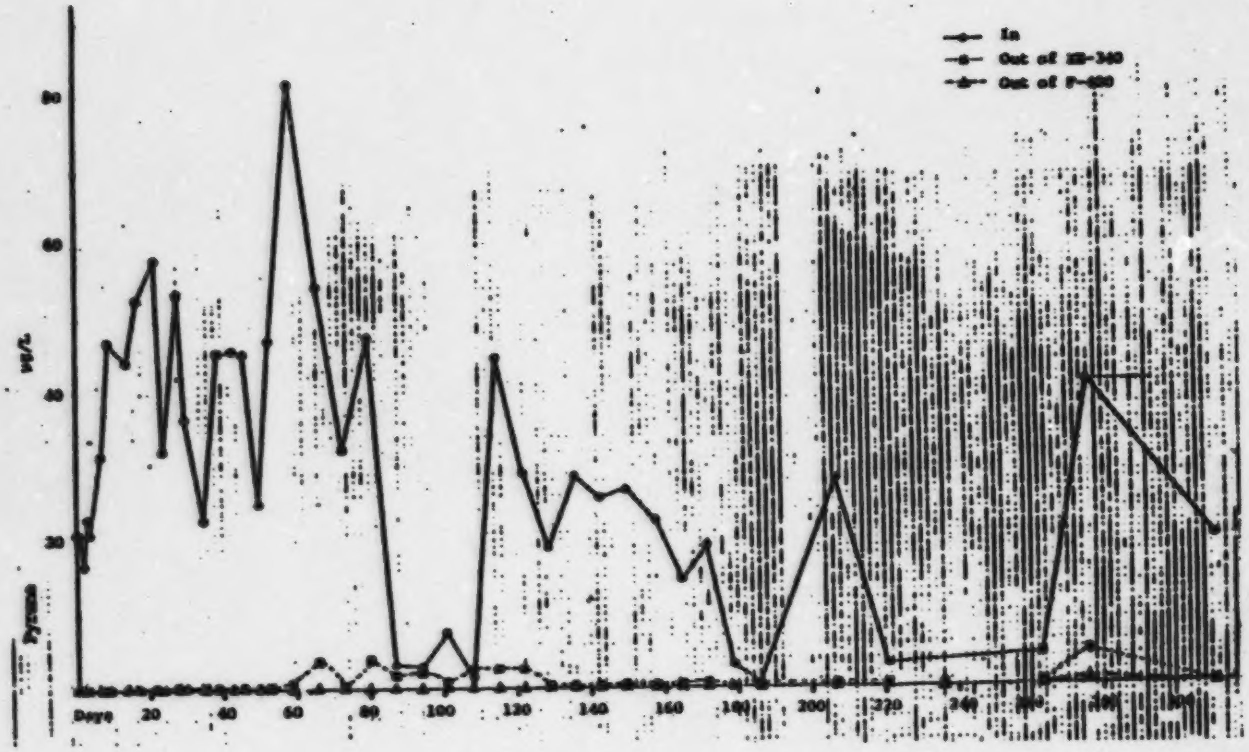


Figure 33 Pyrene influent and effluents in Study A.

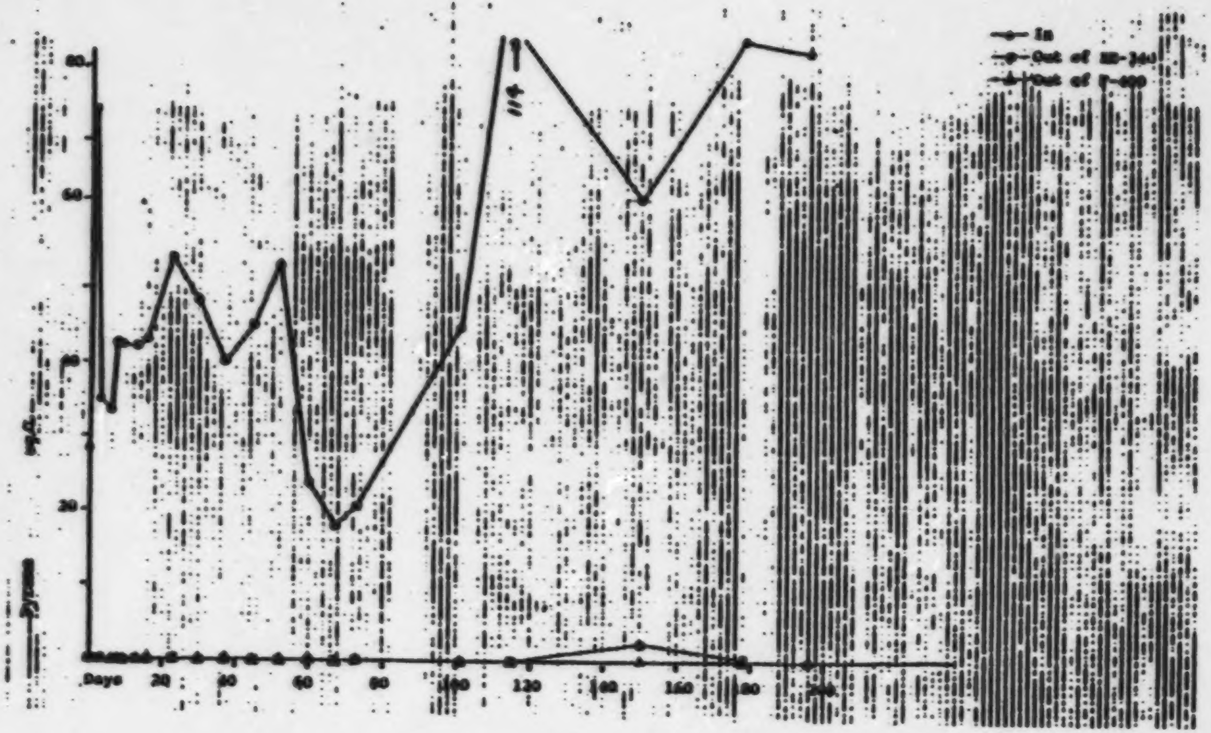


Figure 34 Pyrene influent and effluents in Study B.

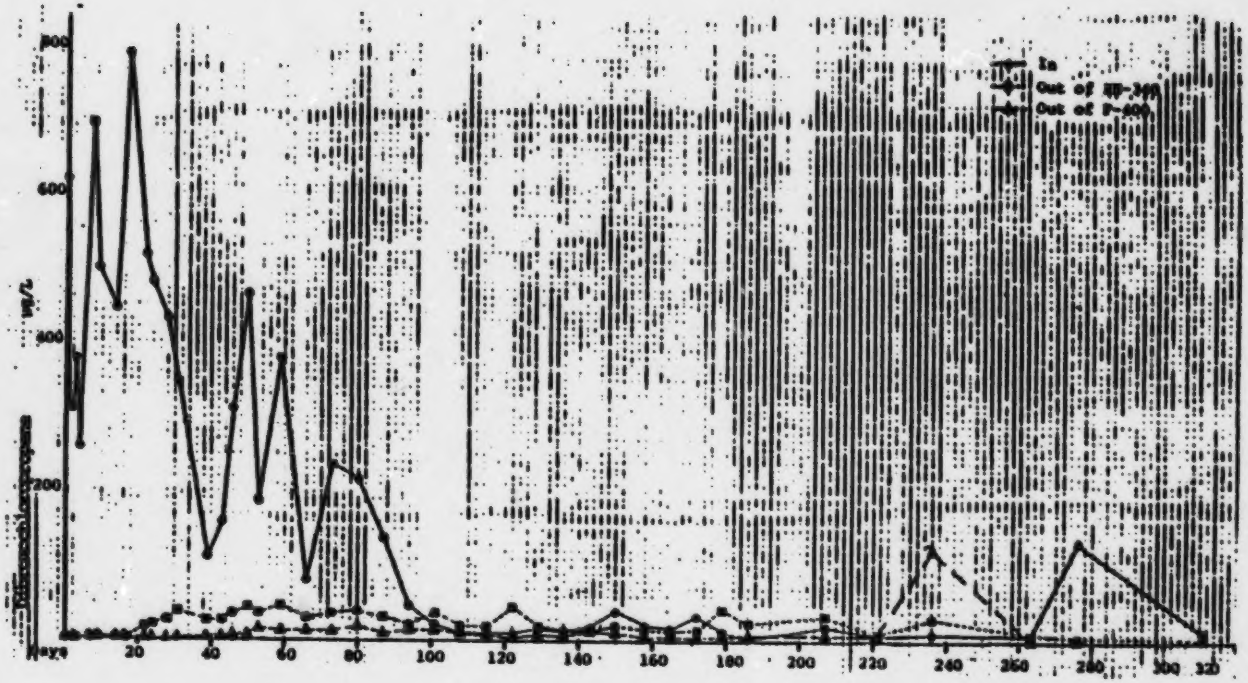


Figure 35 Dibromochloropropane influent and effluents in Study A.

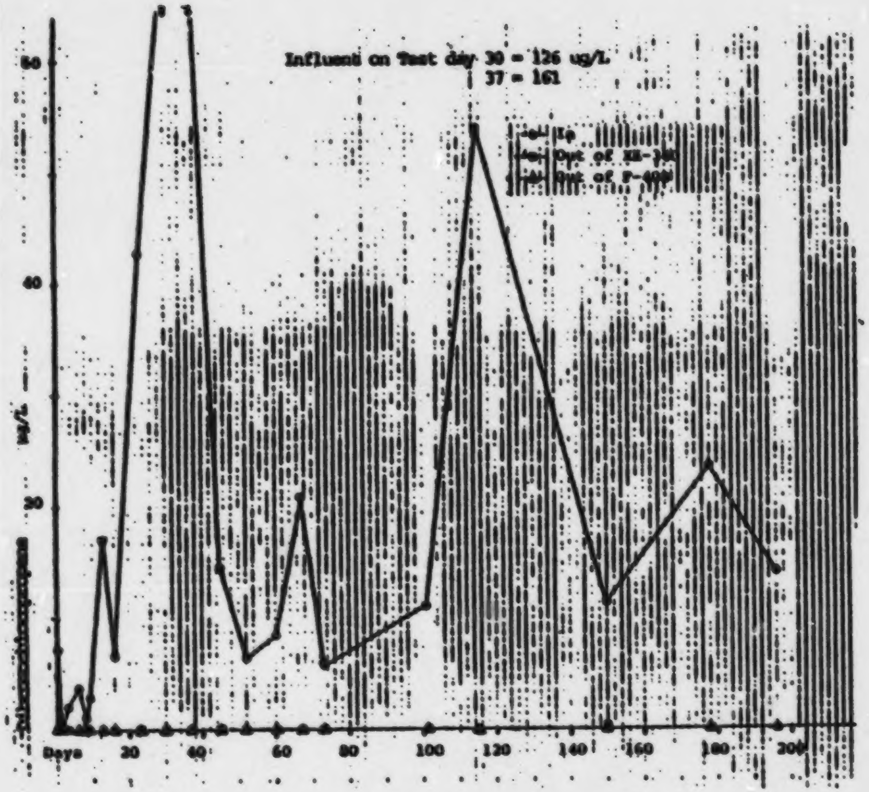


Figure 36 Dibromochloropropane influent and effluents in Study B.

### GAC Results -

In Study A, the GAC column received 3.154 grams of DBCP. The GAC column effluent contained no DBCP to test day 24. From day 24 to the end of the test, the average concentration of DBCP in the effluent was 8.5 µg/L. The column in Study B received 0.3842 grams of DBCP and only intermittent low levels were observed in the effluent over the test period. In Studies A and B, the GAC columns removed 94.3 percent and 99.006 percent of the entering DBCP over the entire test periods.

### XE-340 -

In Study A, breakthrough occurred on test day 9. The average concentration in the effluent averaged 25.4 µg/L from day 9 to the end of the test. At the end of the test period, the column had retained 81.5 percent.

Hexachlorobenzene
α BHC
γ BHC
Pentachloronitrobenzene
Aldrin
Heptachlor

### GAC, XE-340 Results -

The summarized data for the above six chlorinated pesticides in Table 30 needs little further discussion. Data are plotted in Figures 37 through 42. In all cases with both GAC and XE-340 columns, there was slight bleed through the columns over the entire test period. The level was always higher from the XE-340 column. Each column received a total of 0.15174 grams of all six pesticides added together. The poorest adsorption by GAC occurred with Aldrin, 95.3 percent still retained at the end of the test. The poorest adsorption by XE-340 was with pentachloronitrobenzene, 91.3 percent still retained. In all cases, the retention was greater for GAC. The best adsorption by GAC was with BHC, 99.95 percent retained. The best adsorption by XE-340 was with BHC, 98.9 percent retained. These results were obtained with influent concentrations ranging from 2.8 µg/L, downward. Refer to Table 30 and Figures 37 thru 42 for details.

## PCB

### GAC, XE-340 Results -

Arochlor 1254 was studied. The influent loading averaged 1.53 µg/L, resulting in a total loading per column of 0.0397 grams. Low level bleed occurred throughout the test period for both columns. At the end of the test, GAC retained 97.5 percent and XE-340 retained 94.6 percent. Refer to Table 30 and Figure 43 for details.

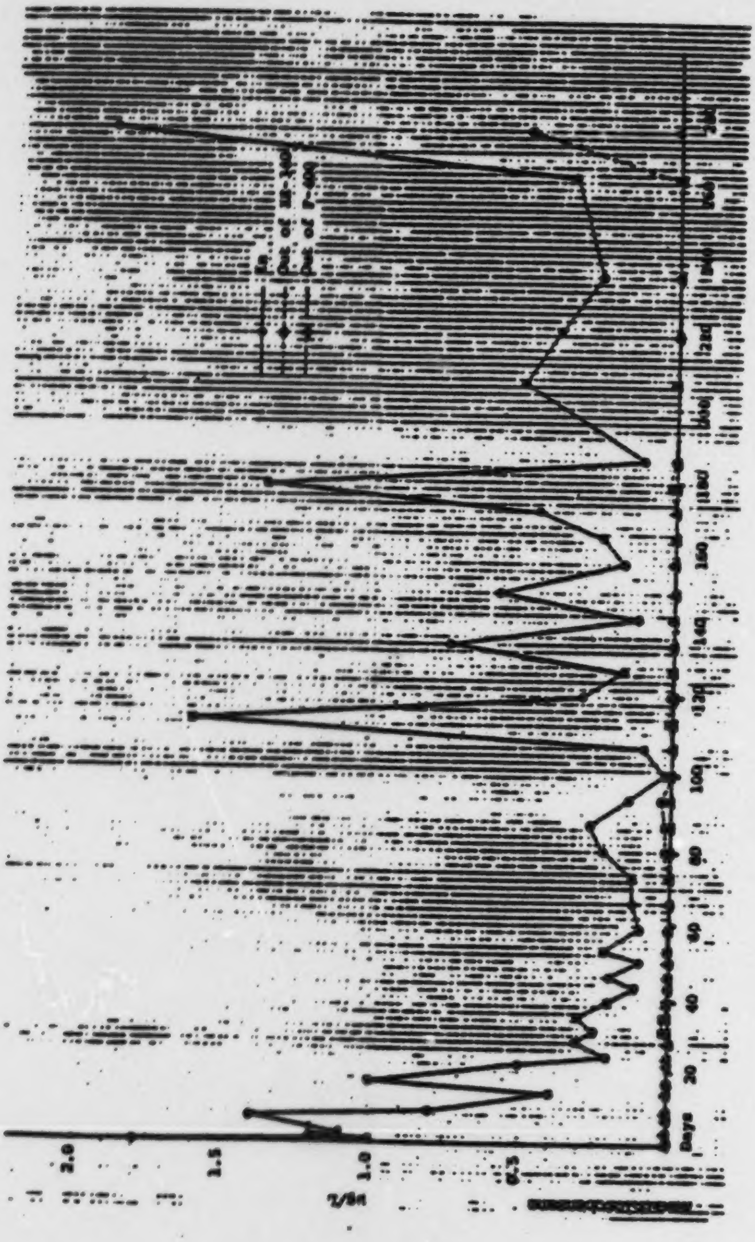


Figure 37 Hexachlorobenzene influent and effluents in Study A.

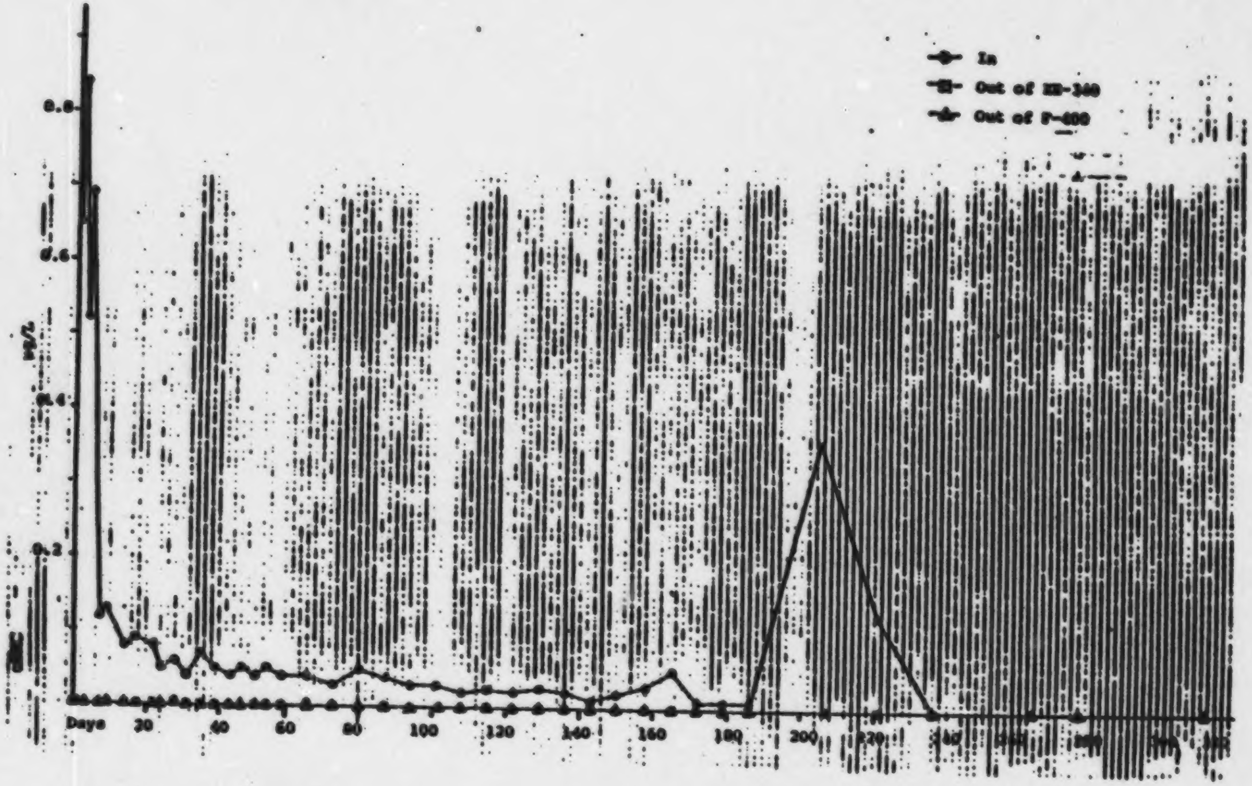


Figure 38 αBHC influent and effluents in Study A.

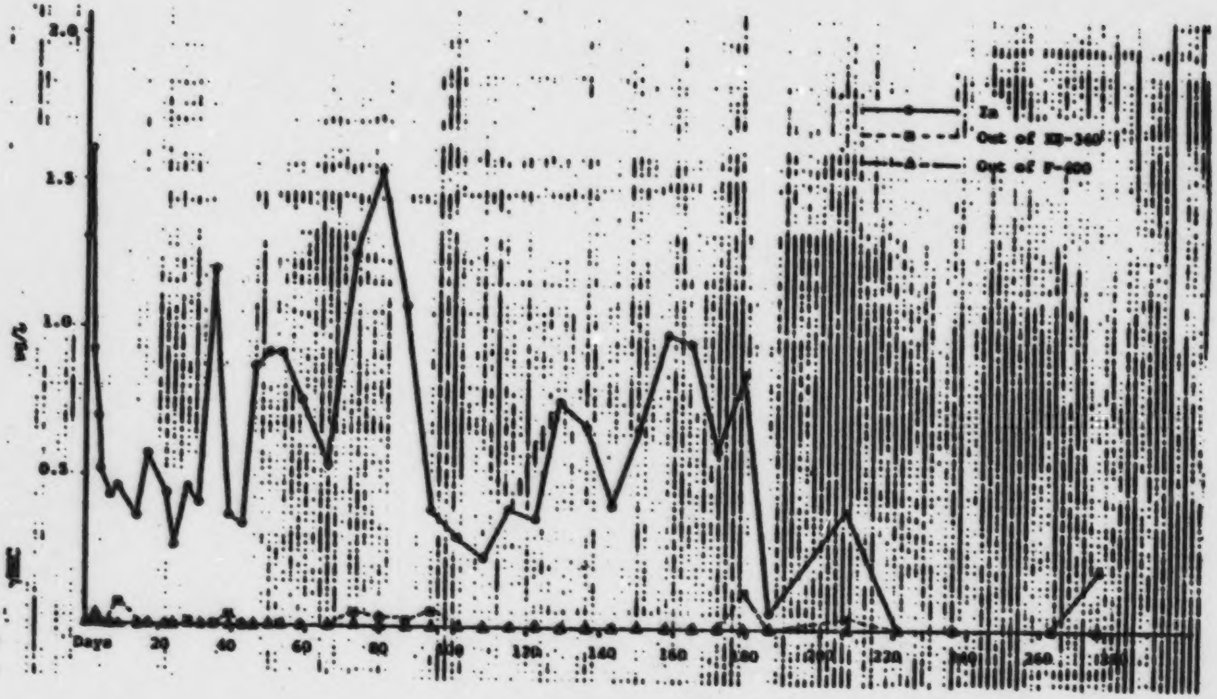


Figure 39 γBHC influent and effluents in Study A.

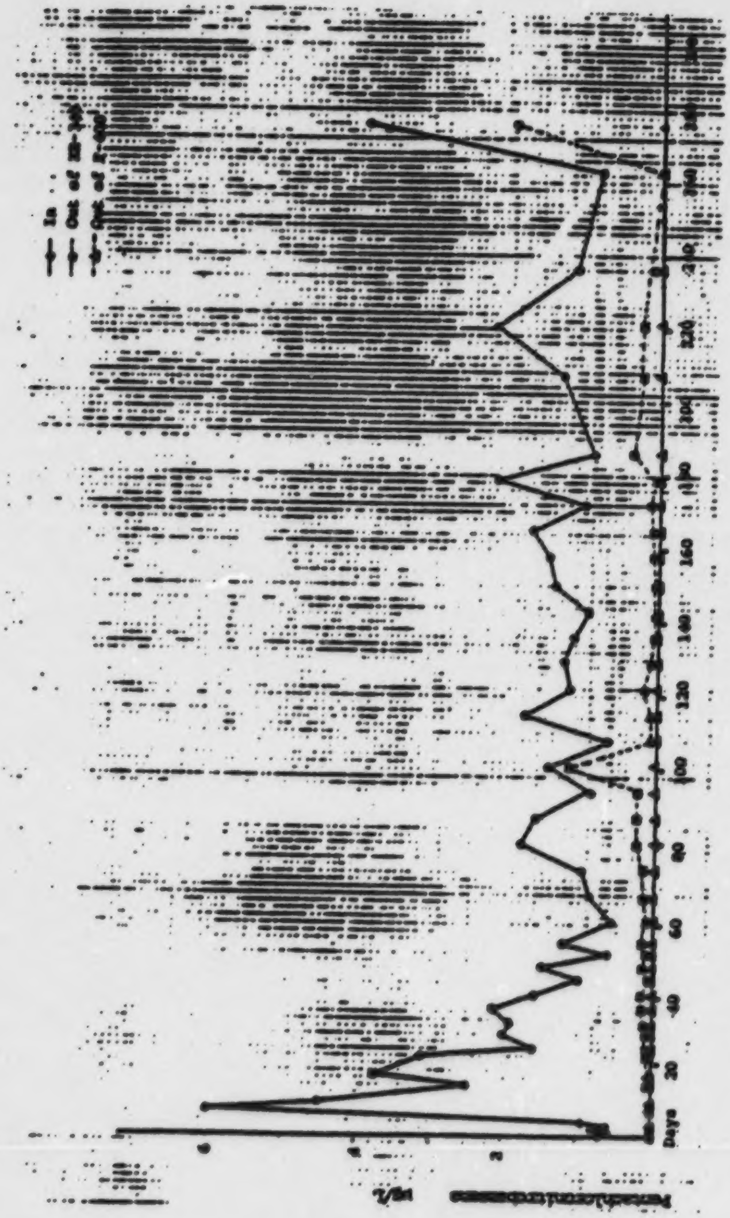


Figure 40 Pentachloronitrobenzene influent and effluents in Study A.

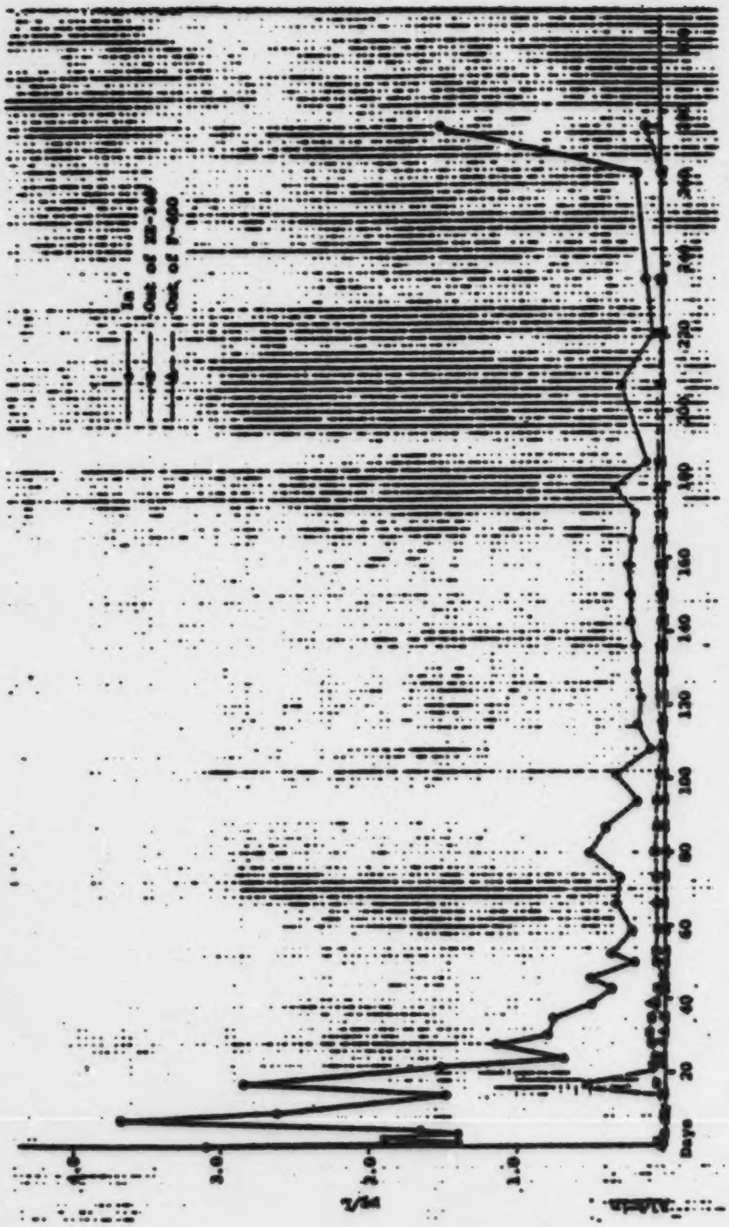


Figure 41 Aldrin influent and effluents in Study A.

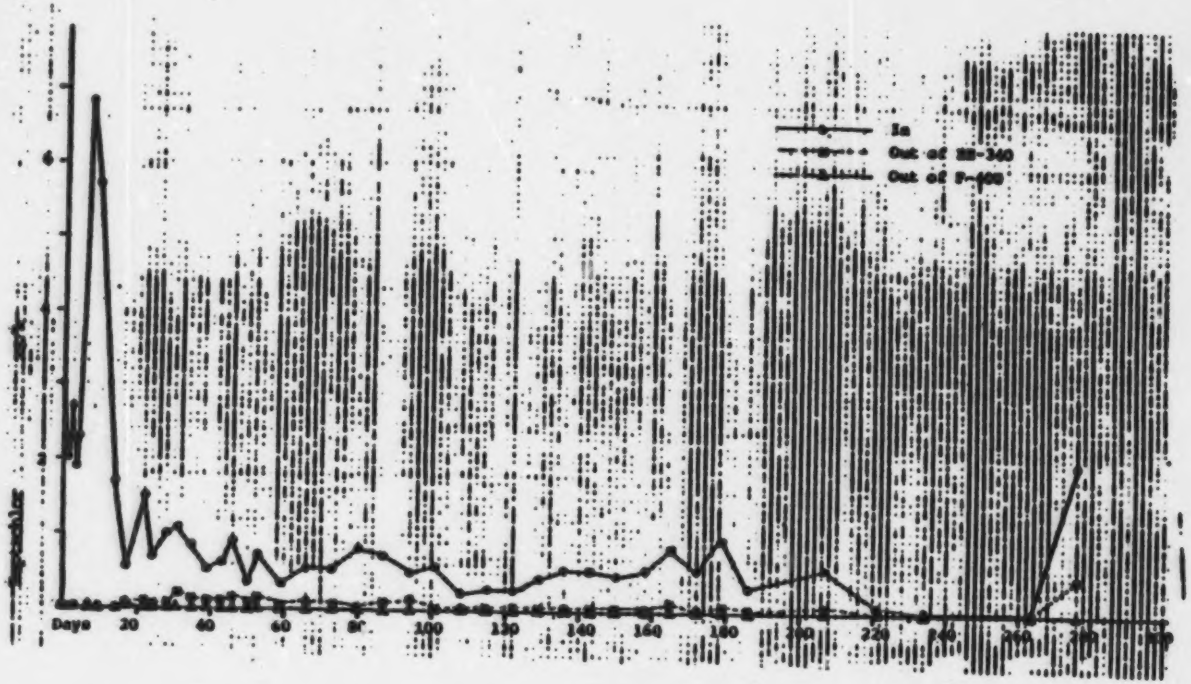


Figure 42 Heptachlor influent and effluents in Study A.

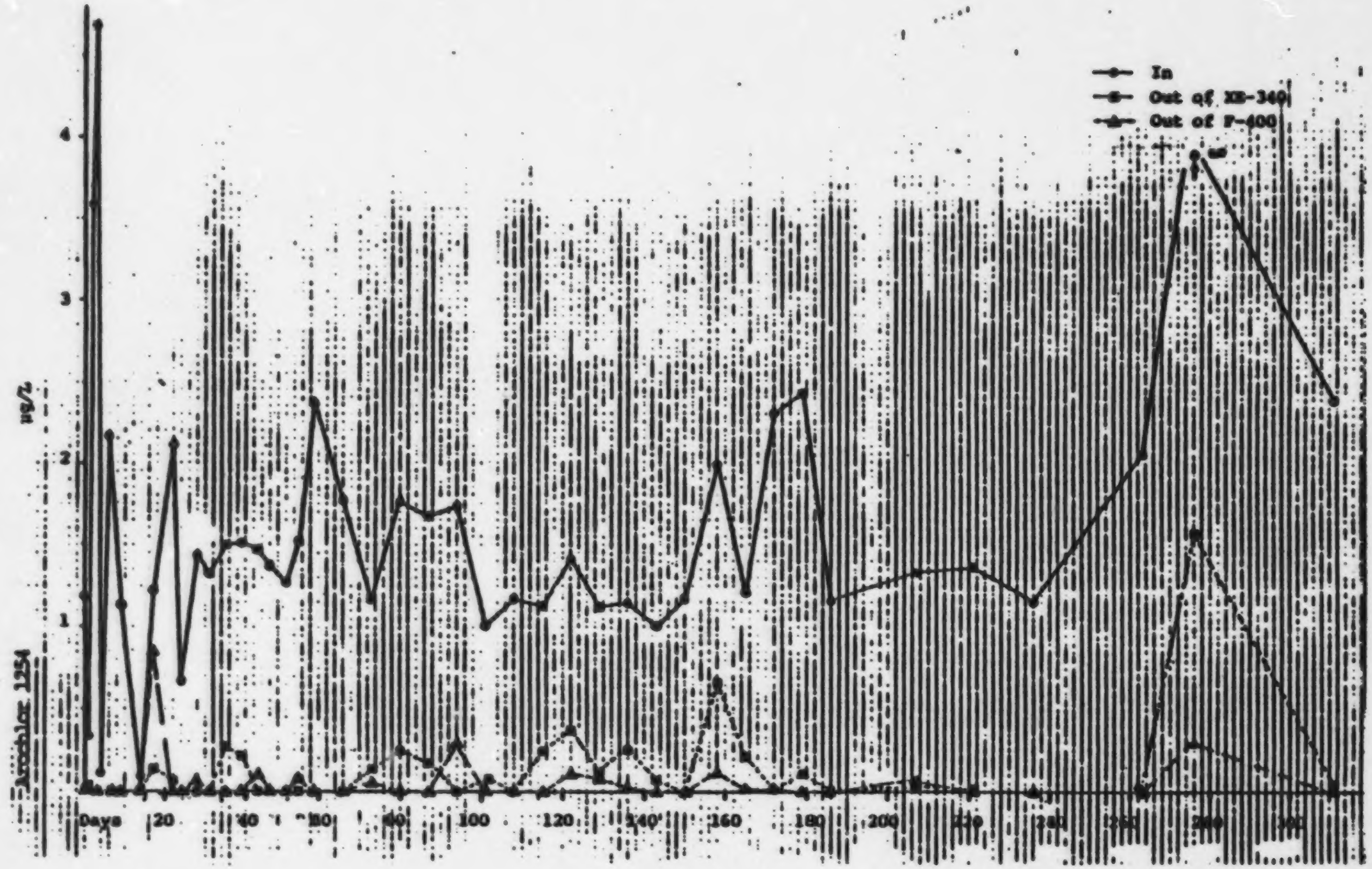


Figure 43 Arochlor 1254 (PBC) influent and effluents in Study A.

## A228 Conclusions from Bench-Scale Unit 2

1) Methods of spiking a wide range of organic compounds, representative of many classes of compounds in the EPA priority pollutant list, were devised to study actual adsorption from finished water by adsorbent columns.

2) Data show how specific units continuously supply various concentrations of each compound at rather uniform constant rates for up to 335 test days. Some spiking units produced decreasing concentrations.

3) From the spiking units described and their data, one could probably devise their own unit to deliver whatever spiking concentration was required for compounds not included in this study.

4) Two adsorbents (2.5 ft. deep) were studied. EBCT was 6.2 minutes, increasing to 12.4 minutes toward the end of testing. The GAC was F-400 (176 grams) from Calgon. The resin was XE-340 (215 grams) from Rohm and Haas. The adsorptive capacity of a specific substance by an adsorbent is dependent on the influent concentration of the substance and competitive adsorption of all other substances present. Therefore, we carefully describe the non-spiked organic loading and variations in specific organic loading over the entire testing periods. Because of the complex interactions involved, the reader must look at all the actual data for specific conclusions. Even then, such conclusions apply specifically to our particular water system. Care should be taken in predicting results in other systems.

5) While the performance of GAC was always better than XE-340, we should consider the following:

a. The mass transfer zone for many of the compounds was at or slightly beyond the 2.5 feet of XE-340 adsorbent depth.

b. Comparison of the two adsorbents at equal but deeper bed depths would reduce the magnitude of differences shown in Conclusion 5 above.

6) Summarized percent removal results are shown in Table 31.

## A23 Additional Spiking Unit Design

At the beginning of the spiking work we experimented with various apparatus designs on specific compounds and then actually measured the uniformity and spiking concentration achieved. A discussion of this work may be of aid to anyone wishing to build their own spiking units.

Working with a water flow rate of one gal/hr we obtained the following average spiked concentrations from the unit described. The spiking units were Swagelok 1/4" tees connected in series so the straight portion of each tee (parallel to the floor) carried the influent water.

The side arms of the tees pointed down toward the floor. The side arm fitting contained a 1/4" O.D. glass tube (1/8" I.D.), 4 inches long and heat sealed at the bottom. The glass tube on each tee contained one compound carefully placed in the bottom of each tube. We only chose compounds heavier than water, either liquid or solid.

TABLE 31

SUMMARIZED PERCENT REMOVAL

| COMPOUND | PERCENT REMOVED | | | |
|---|---|---|---|---|
| | XE-340 | | GAC F-400 | |
| | WATER A | WATER B | WATER A | WATER B |
| **PAH'S** | | | | |
| naphthalene | 64 | 95.6 | 99.4 | 100 |
| acenaphthene | 86.3 | 98.3 | 100 | 100 |
| fluorene | 98 | 98.9 | 99.5 | 100 |
| anthracene | 97.2 | 100 | 100 | 100 |
| phenanthrene | 94.4 | 99.7 | 100 | 100 |
| fluoranthene | 93.6 | 99.0 | 100 | 100 |
| pyrene | 96.5 | 99.7 | 100 | 100 |
| **Chlorinated Pesticides** | | | | |
| dibromochloropropane (DBCP) | 81.5 | 99.4 | 94.3 | 100 |
| hexachlorobenzene | 98.6 | | 99.9 | |
| α BHC | 98.7 | | 100 | |
| γ BHC | 98.9 | | 99.8 | |
| pentachloronitrobenzene | 91.3 | | 99.9 | |
| aldrin | 92.5 | | 95.3 | |
| heptachlor | 97.6 | | 99.8 | |
| **PCB** | | | | |
| Arochlor 1254 | 94.6 | | 97.5 | |

Decreasing the length of the glass tube resulted in higher spiked levels. Increasing the glass tube diameter also increased the spiked levels. Glass tubes up to 1/2" O.D. were studied. Tables 32 and 33 illustrate some of our results.

## TABLE 32

## SPIKING UNIT RESULTS WITH VARIOUS COMPOUNDS (μg/L)

| COMPOUND | AVERAGE SPIKED CONCENTRATION |
|---|---|
| αBHC | 0.006 |
| γBHC | 0.002 |
| chlordane | 0.005 |
| heptochlor-epoxide | 0.016 |
| dieldrin | 0.007 |
| oxychlordane | 0.003 |
| 2-nitrotoluene | 0.08 |
| ethyl benzoate | 0.12 |
| naphthalene | 0.6 |
| 1-chloro-2-nitrobenzene | 0.06 |
| dimethylphthalate | 0.15 |
| di-isobutylphthalate | 0.15 |

## TABLE 33

## SPIKING UNIT RESULTS WITH LARGER DIAMETER GLASS TUBES

| COMPOUND | CONCENTRATION μg/L TUBE DIAMETER O.D. AND LENGTH | |
|---|---|---|
| | 3/8" O.D. BY 1' | 1/2" O.D. BY 1-1/2" |
| 2-nitrotoluene | 0.24 | 2.4 |
| ethylbenzoate | 0.042 | 1.9 |
| naphthalene | 0.026 | 0.18 |
| 1-methyl naphthalene | 0.0072 | 0.13 |
| biphenyl | 0.0056 | 0.047 |

Good results were also achieved with compounds lighter than water (hydrocarbons and aromatic compounds) by placing the side arm tee tube toward the ceiling.

Another spiking unit, shown in Figure 44 was devised. By varying the inner tube diameter we could easily control the effluent spiking concentration. The following results were obtained with ethyl benzoate (water flow rate 1 gal/hr). The average concentration for 1/16, 1/8 and 1/4 inch tubes was 1.8, 1.5 and 0.062 μg/L.

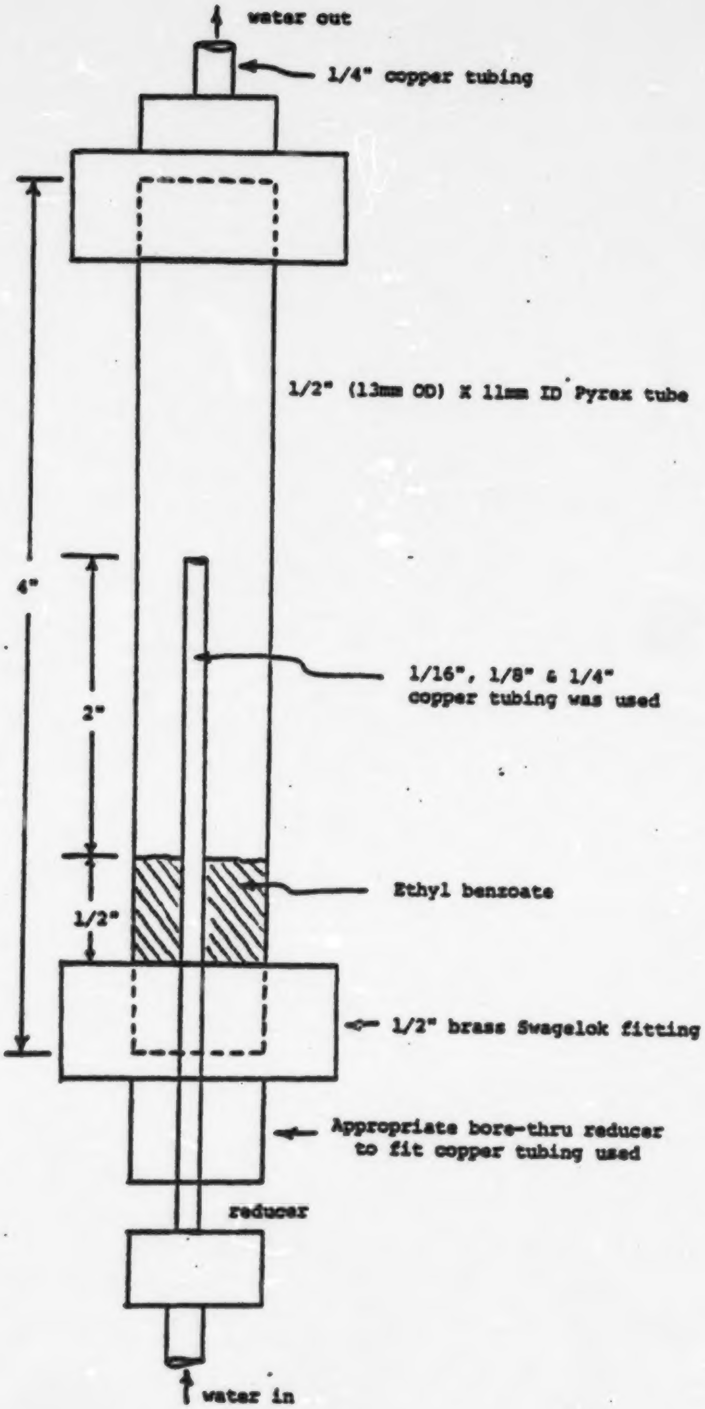

water out
1/4" copper tubing
1/2" (13mm OD) X 11mm ID Pyrex tube
4"
2"
1/16", 1/8" & 1/4"
copper tubing was used
Ethyl benzoate
1/2"
1/2" brass Swagelok fitting
Appropriate bore-thru reducer
to fit copper tubing used
reducer
water in

Figure 44 Variable control spiking unit.

# APPENDIX B

## EXPERIMENTAL DESIGN 2:
## USING AERATION TO REMOVE THMFP

### B1 Introduction

The objective of this study was to learn more about the parameters affecting aeration loss from water of a selected group of volatile organic contaminants common to drinking water throughout the United States. These compounds comprise mostly the low molecular weight halogenated compounds of one and two carbon molecules. We have shown (Ref. 1) that such compounds can be removed by adsorbents but effective bed life is short. The work also includes chlorinated benzenes and benzene itself.

The literature contains aeration work which is largely summarized by Symons et al. (Ref 17). Liss and Slater (Ref 18) studied the flux of gases across the airsea interface. Mackay and Leinonen (Ref 19) expanded on this approach. Cohen, Cocchio and Mackay (Ref 20) studied the effect of wind velocity over the water surface. Mackay, Shiu and Sutherland (Ref 21) studied the effect of gas to water ratio on evaporation in a laboratory purging apparatus. Dilling, Tefertiller and Kallos (Ref 22) and Dilling (Ref 23) studied evaporation from a stirred beaker.

### B2 Equations

Liss and Slater (Ref 18) refer to a two-layer model of an air-water interface in deriving equations for the loss of compounds across the interface. In their equation they caluclate a Henry's Law constant ($H_i$) as follows:

$H_i$ = a Henry's Law constant (atm $m^3$/mol)

$$H_i = \frac{P_i}{C_{is}} \qquad (1)$$

where $P_i$ = vapor pressure of compound i (atm)

$C_{is}$ = solubility of compound i in water (mol/$m^3$)

Dilling (Ref 23) calculates the Partition Coefficient, Henry's Law Constant as follows:

$$H_{iPC} = \frac{C_i \text{ air}}{C_i \text{ water}} = \frac{16.04 \text{ PM}}{\text{TS}} \qquad (2)$$

where $H_{iPC}$ = Partition Coefficient, Henry's Law Constant at equilibrium (dimmensionless)

$C_i$ air = equilibrium concentration of compound i in air
$C_i$ water = equilibrium concentration of compound i in water
P = vapor pressure of compound i in mm of Hg
M = gram molecular weight of compound i
T = temperature in K°
S = solubility of compound i in water mg/L

$$16.04 = \frac{1000}{760(.082)}$$ a factor based on the units chosen above

The Partition Coefficient can also be determined as follows:

$$H_{iPC} = \frac{H_i}{RT} \qquad (3)$$

In this report, we use Dilling's equation (2) for calculating the Partition Coefficent, $H_{iPC}$.

## B3 Aeration from a Stirred Beaker

### B31 Preparation and Behavior of Single and Multiple Organic-Water Mixtures

### B311 Method of Spiking

In the initial work with both beaker and aeration tower studies, it soon became apparent that when spiking organics into water, utmost care had to to be taken that all spiked compounds were completely soluble. At one time we even questioned that the rate-loss of a single compound from water might be different from the rate-loss of the same compound when several other compounds were also present. Our initial aeration work began with aeration tower studies, but erratic results prompted a turn to beaker studies where with precise controls we then confirmed that the rate-loss of a single compound was the same regardless of the presence of other compounds, as long as all compounds were completely soluble. In this work, it was found that if the pure compound was injected as a liquid into water; e.g., 0.1 µL of chloroform equals approximately 150 µg in one liter of water, over 24 hours was required, with constant stirring, for complete solution to occur. With compounds such as carbon tetrachloride and tetrachloroethylene, more than three days were required. If a more concentrated solution in methanol was made, such that no more than one milliliter of methanol standard was added to one liter of water, solution occurred more rapidly because microdroplets were formed; but even with this, several days of constant stirring was necessary when the more insoluble compounds were added. Erratic results ended when a good system of spiking both large and small amounts of water was established. The estalished method worked for spiking from 250 gal. to one liter of water which were suitable volumes for aeration tower and beaker study work, respectively. In both cases the single or multi-component organics were first dissolved in methanol and then the methanol concentrate was added to water. The ratio of methanol to final volume of water was never more than one ml of methanol to one liter of water. Several times this much alcohol might not alter the results. This ratio was just never exceeded after it was found by testing that this ratio did not alter the rate-loss data compared to spiked water using no alcohol.

For the beaker studies, requiring a total of one liter of water, the right amount of each pure liquid, in uL, was added to make a 100 ml methanol concentrated standard. One ml of this standard was then added to the water. Best results were obtained using a Corning Pyrex 1500 reagent bottle, narrow mouth; improved ST stopper, Cat. No. 1500-IL. A Teflon-coated magnetic stirring bar was placed in the bottle with most of the water. After adding the one ml of concentrated standard, the bottle was filled with water and the glass stopper pushed in place with no air head space. The bottle was then placed on a magnetic stirrer with two layers of corrugated cardboard between the bottle and top of the stirrer plate to prevent slight heating of the water. To be sure of complete solution, stirring was continued for several days. The reagent bottle actually held approximately 1100 ml. To run the beaker test, exactly 1000 ml of water was placed in the beaker (jar) and the stirrer speed was adjusted. After approximately 10 minutes of stirring, the first sample (10 ml) was taken and sealed with no head space in a septum vial.

For spiking water in the aeration tower work, the above method was repeated using two five-gallon glass bottles with approximately a one-inch diameter opening. The contents of the two five-gallon bottles were then thoroughly mixed with the water in the holding tank.

### B312 Beaker Apparatus

The apparatus used for this work is shown in Figure 45. The stirring paddle was one of the paddles on a six-paddle stirrer from Phipps and Bird, Inc., commonly used for coagulation jar test studies. The stirring speed was 100 rpm. Water and air temperature was 22°C (76°F). Air currents were those found in the normal laboratory environment.

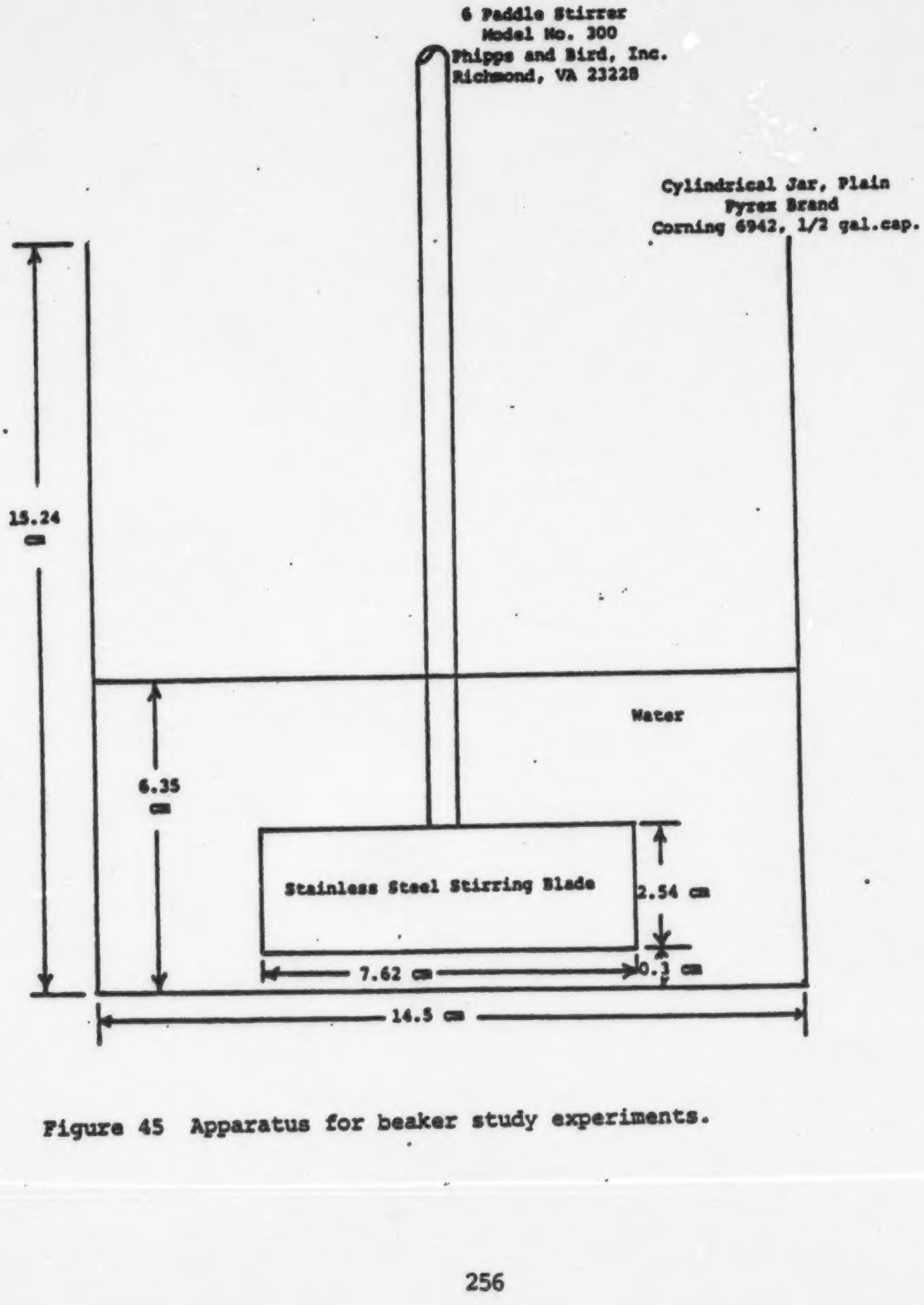

6 Paddle Stirrer
Model No. 300
Phipps and Bird, Inc.
Richmond, VA 23228
Cylindrical Jar, Plain
Pyrex Brand
Corning 6942, 1/2 gal.cap.
15.24 cm
Water
6.35 cm
Stainless Steel Stirring Blade
2.54 cm
7.62 cm
0.3 cm
14.5 cm

Figure 45 Apparatus for beaker study experiments.

## B313 Behavior of Individualy and Grouped Spiked Compounds in Beaker Study

### Test 1

The data in Table 34 show the rate-loss in µg/L against time in the beaker study for compounds tested as a group and individually and without the aid of methanol. The data show, by half life and slope values, that there is no difference in rate-loss when tested individually or in a group and whether or not methanol was used. Note that in all cases the maximum concentration of any compound was only a fraction of a percent of its maximum solubility; e.g., carbon tetrachloride was a maximum of 0.004 percent. Later in this report on aeration studies we show that rate-loss does not change even when the total soluble spiked level of many compounds reached nearly 5000 µg/L.

### Test 2

In Test 2, rate-loss data (µg/L versus time) for nine halogenated organics are shown in Table 35. These data are plotted in Figures 46 and 47. As shown by Mackay, Shiu and Sutherland (Ref. 21), the plot of log concentration against time is linear. Physical data calculated from these linear plots are shown in Table 35.

In Figures 46 and 47, the half life of each compound can be determined directly from each curve. The half life is the time required for the initial concentration (or the concentration at any point) to decrease by one-half. For example, in Figure 46, the initial concentration of chloroform was 52 µg/L (also from Table 35), one-half of this value is 26 µg/L. Project, from the Y-axis, a line from 26 to the chloroform linear curve and then down to the X-axis, reading a half life of 51 minutes (as shown in Table 36). Since the plot for each compound is linear, it doesn't matter where we take the initial concentration along the curve. Without specific air-water interface equations, we can also determine the slope of each linear plot. The slope equals Y/ X or:

$$\text{Slope} = \frac{\log C_i - \log C_{i0}}{t_2 - t_1} \qquad (4)$$

where $t_1$ = initial time corresponding to $C_{i0}$
$t_1$ = time corresponding to $c_i$

# TABLE 34

## RATE-LOSS DATA FOR HALOGENATED ORGANICS FROM BEAKER STUDY VARYING SPIKING CONDITIONS (TEST 1)

| | | µg/L | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Init. Conc. | 5 min. | 10 min. | 20 min. | 30 min. | 90 min. | half life in min. | half life in hours | slope |
| methanol (group) | carbon tetrachloride | 54 | 43.5 | 33.1 | 32.8 | 25.2 | 4.5 | 25.7 | 0.428 | 1.619 |
| | chloroform | 65.4 | 57 | 50.2 | 43.1 | 32.3 | 8.2 | 29.2 | 0.487 | 1.423 |
| | bromodichloromethane | 63 | 56 | 54 | 44.5 | 36.1 | 11.7 | 41.5 | 0.691 | 1.003 |
| | chlorodibromomethane | 68.3 | 62.8 | 59.8 | 51 | 45 | 14.8 | 42.7 | 0.711 | 0.975 |
| | bromoform | 62.8 | 56.8 | 54 | 44.5 | 40 | 17.5 | 48 | 0.8 | 0.866 |
| methanol (individual) | carbon tetrachloride | 174.8 | 148 | 120.1 | 105 | 78.3 | 14.8 | 24.8 | 0.413 | 1.678 |
| | chloroform | 120 | 105 | 98.2 | 74 | 58.2 | 16.5 | 30 | 0.5 | 1.366 |
| | bromoform | 130.2 | 124 | 119 | 102 | 80.1 | 31 | 46.2 | 0.77 | 0.900 |
| Water (group) | carbon tetrachloride | 103 | 90.2 | 84.1 | 56.3 | 49 | 10.5 | 26.7 | 0.438 | 1.582 |
| | chloroform | 85.1 | 74 | 63.8 | 54.1 | 38 | 8.6 | 28.3 | 0.472 | 1.468 |
| | bromodichloromethane | 73.8 | 66 | 60.2 | 53.2 | 43.3 | 15.6 | 42.5 | 0.708 | 0.979 |
| | chlorodibromomethane | 79.6 | 74 | 66.1 | 60.2 | 51 | 18.3 | 44.5 | 0.742 | 0.934 |
| | bromoform | 109.7 | 100.3 | 93.1 | 82 | 67.9 | 32.1 | 47.3 | 0.788 | 0.880 |
| Water (individual) | carbon tetrachloride | 92.3 | 83.2 | 67.2 | 56.5 | 37.3 | 80.6 | 25.0 | 0.417 | 1.662 |
| | chloroform | 148 | 130.3 | 115.8 | 92.2 | 77.3 | 16.6 | 29.5 | 0.492 | 1.409 |
| | bromoform | 75.8 | 69.9 | 67.2 | 54.3 | 51.5 | 24.3 | 46.8 | 0.78 | 0.889 |

## TABLE 35

## RATE-LOSS DATA FOR HALOGENATED ORGANICS FROM BEAKER STUDY APPARATUS (TEST 2)

| | μg/L | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform |
| Initial Conc. | 112 | | | | 74 | 32 | | 140 | 58 | 124 | 79 | | 134 | | 108 |
| 30 min. | 60.2 | | | | 52.3 | 29.5 | | 81.3 | 32.6 | 73 | 46.3 | | 63.8 | | 72 |
| 90 | 22 | | | | 24 | 16.2 | | 30.1 | 19.4 | 33 | 26 | | 39.4 | | 54 |
| 150 | 4.4 | | | | 8.8 | 5.8 | | 11.2 | 6.2 | 12.1 | 20.6 | | 16.6 | | 33.4 |
| 210 | 3.6 | | | | 3.8 | 0.27 | | 3.1 | 1.4 | 4.6 | 4.3 | | 7.9 | | 13 |
| 270 | 0.77 | | | | 1.5 | 0.33 | | 1.3 | 1.0 | 1.8 | 3.2 | | 5.9 | | 10.2 |
| 330 | nil | | | | 0.92 | 0.68 | | 0.49 | 0.18 | 1.25 | 1.2 | | 1.9 | | 3.2 |

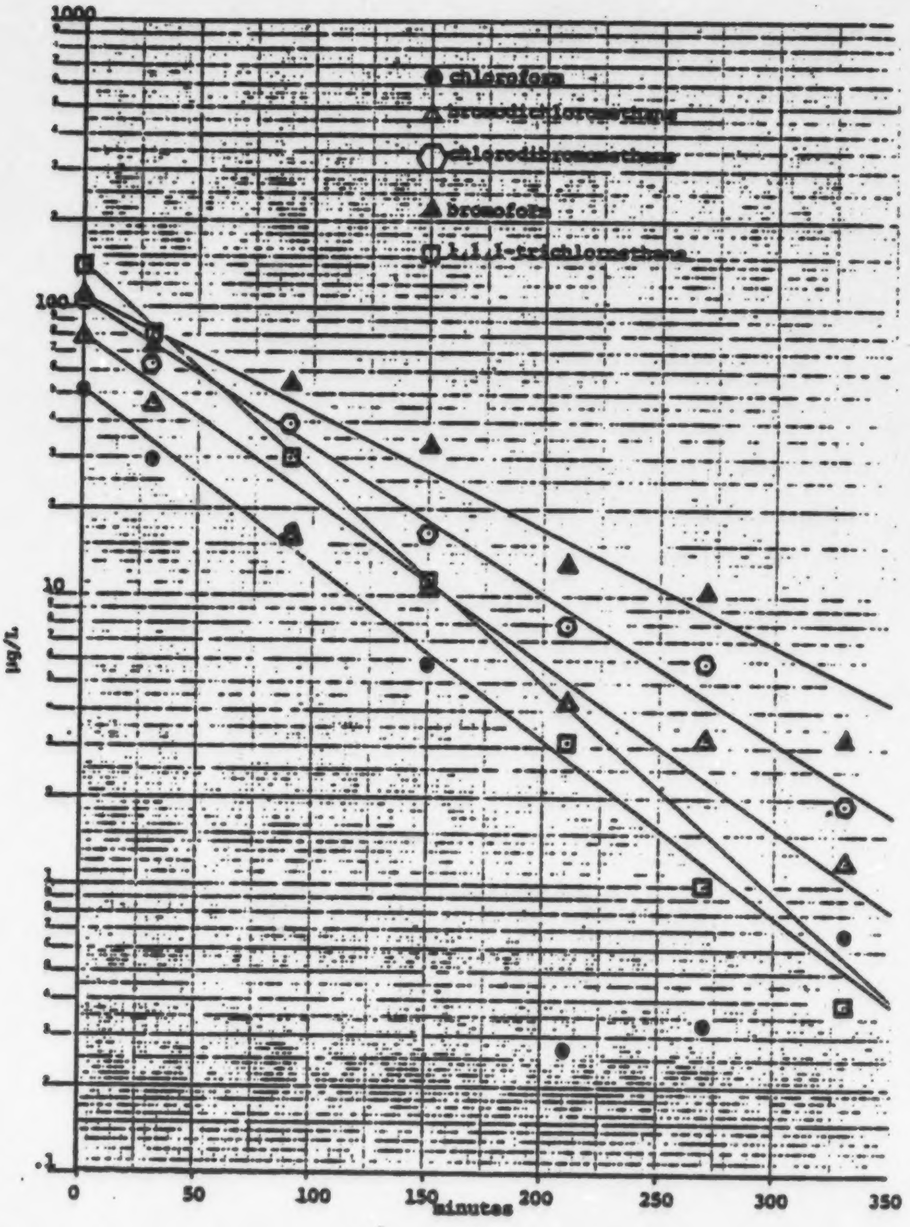


Figure 46 Rate-loss of halogenated organics from beaker study apparatus (Test 2).

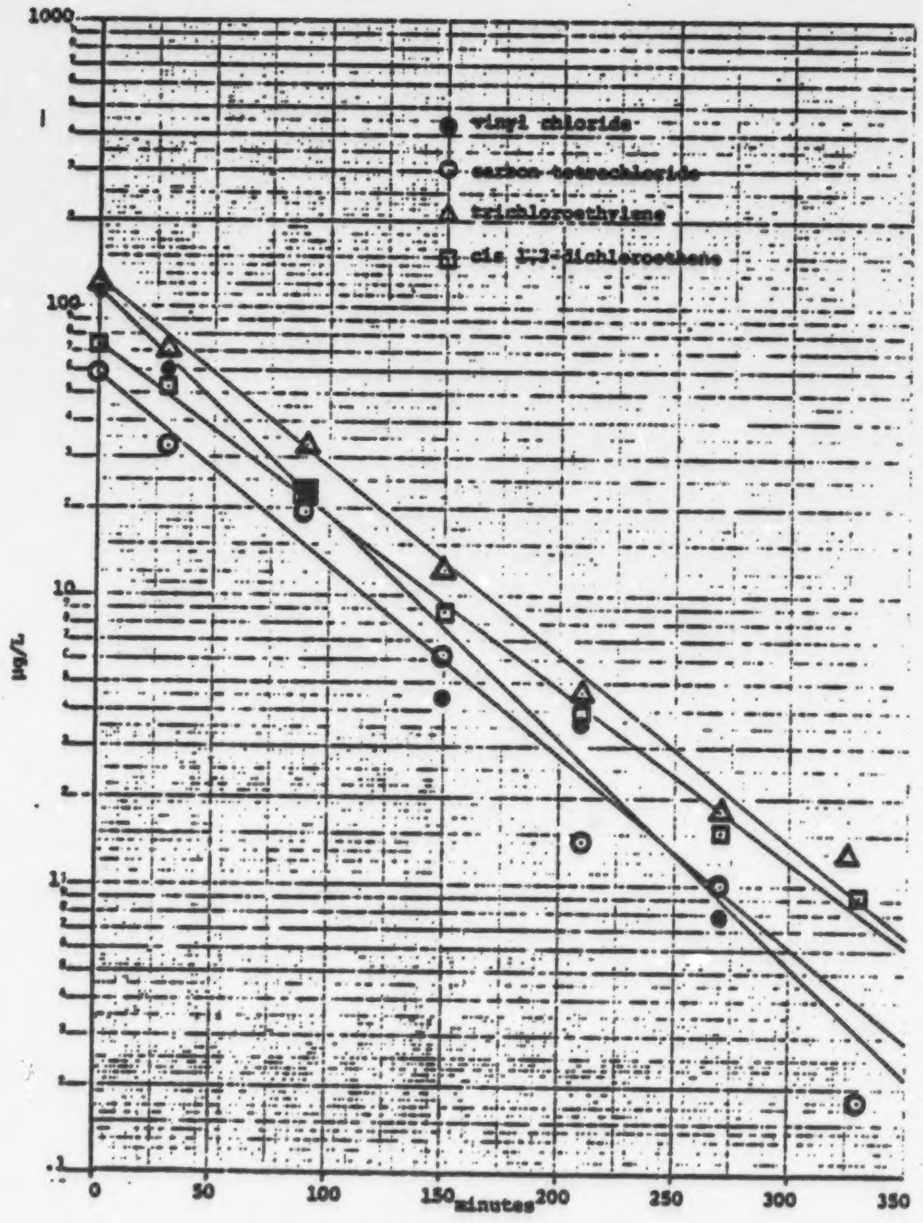


Figure 47 Rate-loss of halogenated organics from beaker study apparatus (Test 2).

## TABLE 36

## PHYSICAL DATA OF HALOGENATED ORGANICS FROM BEAKER STUDY APPARATUS (TEST 2)

| | $H_{iPC}$ | Half life minutes | Half life hours | Slope |
|---|---|---|---|---|
| vinyl chloride | 43*<br>0.955*<br>5.2 Exp. | 39 | 0.65 | 1.07 |
| 1,1,1-trichloroethane | 1.2 | 42 | 0.71 | 0.98 |
| carbon tetrachloride | 0.97 | 45 | 0.75 | 0.924 |
| trichloroethylene | 0.48 | 47 | 0.79 | 0.88 |
| cis 1,2-dichloroethene | 0.29 | 50 | 0.83 | 0.831 |
| chloroform | 0.15 | 51 | 0.85 | 0.815 |
| bromodichloromethane | .099 | 54 | 0.9 | 0.770 |
| chlorodibromomethane | .043 | 60 | 1 | 0.693 |
| bromoform | .023 | 74 | 1.23 | 0.564 |

*Reported by Dilling (Ref. 23)

The compounds tested in this beaker study with their corresponding Henry's Law Partition Coefficient value ($H_{iPC}$) is shown in Table 36. We also show the half life in minutes and hours and the slope of the linear rateloss curve for each compound. The slope values in Tables 34 and 35 differ because beaker test conditions, e.g. temperature and air flow over water surface, were not exactly the same.

In Figures 46 and 47 and Table 36, it is apparent that the slope of the linear plot for each compound is in some way proportional to the Partition Coefficient ($H_{iPC}$). That is, the slope increases as the $H_{iPC}$ increases. The relationship of $H_{iPC}$ to slope is shown by a plot of these two values in Figure 48. Most of the data points fall near a straight line zone. Bromoform, with the lowest $H_{iPC}$ value of 0.023 appears to deviate from the straight line. Possible reasons for this will be discussed later. Dilling (Ref. 23) reports two possible $H_{iPC}$ values for vinyl chloride based on the uncertainty of solubility data for vinyl chloride. The two values, 43 and 0.955 (Table 36), could both be inaccurate. The experimental beaker data, Table 36, indicates an experimental value of 0.65 hours half life and a slope of 1.07. In Figure 48, if we extend the straight line and then plot the vinyl chloride datum point on the extended line corresponding to 1.07 on the X-axis, we read the experimentally determined value of 5.2 for $H_{iPC}$ on the Y-axis.

From Figure 48, one can probably (or at least tentatively) conclude that for a family of compounds (the term "family" to be described later) with $H_{iPC}$ values of approximately 0.043 or above, the plot of log $H_{iPC}$ against slope is a straight line. Therefore, for a beaker test (or perhaps a related system) if one determines the slope of the line by experimentally testing at least two compounds (separated by a reasonable difference in $H_{iPC}$ value), one can experimentally determine the rate-loss for a third compound if its $H_{iPC}$ is known.

In this report, unless otherwise stated, all time is in hours. The slope of the chloroform curve in Figure 46 is therefore:

$$\frac{\log (26\ \mu g/L) - \log (52\ \mu g/L)}{\frac{51}{60}-0} = \frac{-0.301}{0.85} = -0.354$$

The chloroform line has a negative slope of -0.354. Even though plotted on log paper, the slope from equation (4) is really:

$$\text{slope} = \frac{\ln C_i - \ln C_{i0}}{t_2 - t_1} \qquad (5)$$

Therefore, multiplying the negative slope -0.354 by 2.3 gives the ln base slope of -0.815 for the chloroform curve in Figure 46. This slope value is reported in Table 35 (the negative sign is dropped). Of course, equation (5) can also be written:

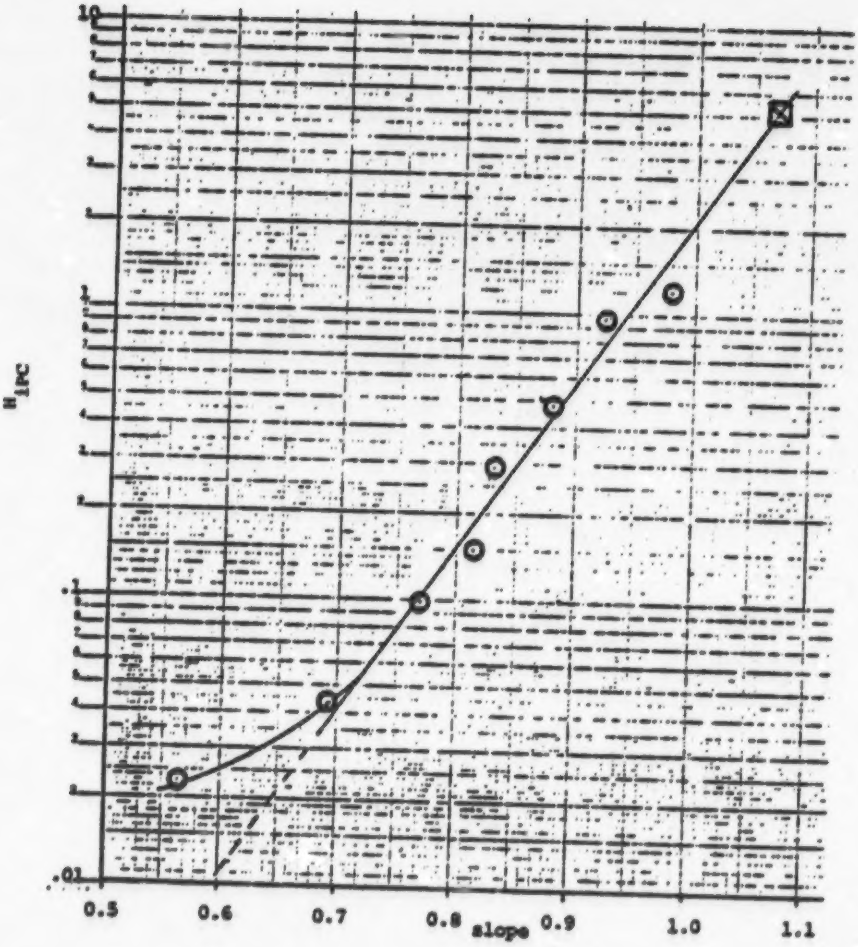


Figure 48 Plot of $H_{iPC}$ versus slope of the linear rate-loss curves for halogenated organics from beaker study apparatus (Test 2).

$$\text{slope} = \frac{\ln \frac{C_i}{C_{i0}}}{t} \qquad (6)$$

where $t = \Delta t = (t_2 - t_1)$

Also, when a point $C_i$ is chosen one-half the value of $C_{i0}$, the corresponding t becomes the half life of the compound $t_{1/2\,L}$. In such a case, ln $C_i/C_{i0}$ becomes 0.693 (the natural log of 0.5). Therefore, it is always convenient to pick $C_i$ equal to one-half $C_{i0}$ to get the half life and equation (5) becomes:

$$\text{slope} = \frac{0.6931}{t_{1/2L}} \qquad (7)$$

## B4 Aeration Tower Study

### B41 Tower Description

The aeration tower used in this study is shown in Figure 49. The outside of the tower was constructed of 5/8 inch exterior plywood, painted with two coats of epoxy paint. The arrangement of the half-inch PVC plastic pipe splash bars was suggested by Argo (Ref. 24). The inside square cross section of the tower was one foot square (1 ft. by 1 ft.). Water was delivered through nine spray heads. These were a conventional home product type used for sinks and available in hardware stores. They were manufactured by Melard Manufacturing Corp., Passaic, N.J. 07055, Part No. 590. The spray openings in the metal disc were one mm diameter. Water flow rate was monitored by a conventional water meter used for homes by the local water utility company. The distance from the spray heads to the first sampling point and top of the first splash bar was approximately six inches. At this first sampling point the aeration loss caused by the spray heads and approximately six inches of free fall could be measured. The next two sample points were after four ft. and eight ft. of splash bar tower section. The total length of splash bar tower section was nine ft. The last foot of this section contained two square openings on opposite sides of the tower (6 inches by 6 inches) to allow air to enter the tower by a chimney effect. The water collection box at the base of the tower was also open to allow air to enter. Water from the collection box was stored in a holding tank (240 gallon capacity).

In the first part of the study 100-gallon glass holding tanks were used, but because they had no bottom drain, the 240-gallon holding tanks were constructed from exterior plywood, incorporating bottom drains.

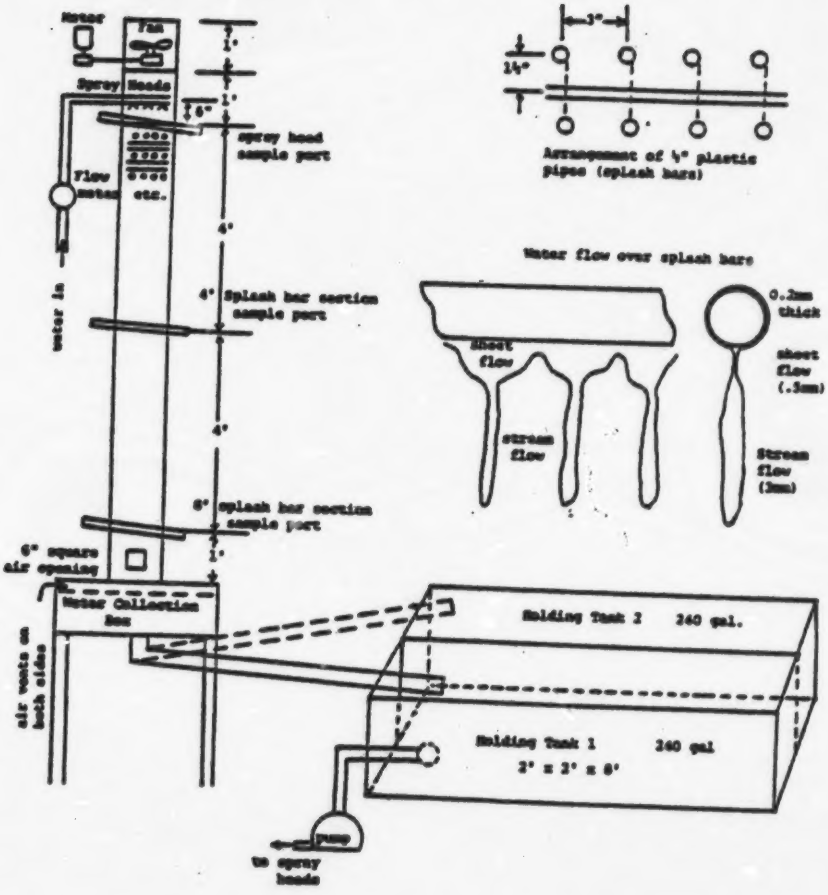

Motor
Fan
Spray Heads
1'
1'
6"
spray head sample port
Flow meter
etc.
water in
4'
4' Splash bar section sample port
4'
8' splash bar section sample port
6" square air opening
1'
Water Collection Box
air vents on both sides
3"
1½"
Arrangement of ½" plastic pipes (splash bars)
Water flow over splash bars
Sheet flow
stream flow
0.2mm thick
sheet flow (.3mm)
Stream flow (3mm)
Holding Tank 2 240 gal.
Holding Tank 1 240 gal
2' x 2' x 8'
pump
to spray heads

Figure 49 Details of aeration tower.

Because leakage through the seams was too great, the interior was fiber-glassed with glass cloth and polyester resin. This resulted in a problem. If the water in the holding tank contained free chlorine, in just 5 to 15 minutes retention, considerable amounts of chloroform was produced by the reaction of free chlorine with the resin coating. Later in the report we will show data on this chloroform growth. The problem was solved by not putting finished water directly through the tower on the first tower pass. Instead, the finished water containing free chlorine was put into one of the holding tanks and treated with sufficient sodium thiosulfate to destroy all the free chlorine. The procedure was then to pass the dechlorinated water, as is or spiked, repeatedly through the tower, into the empty holding tank and then back through the tower into the just emptied holding tank. Five complete passes were usually made through the tower. The fan box was removed for no forced air tests. For forced air test, the air flow was measured at the water flow rate desired. It was observed that an air flow rate of 300 $ft^3/min/ft^2$ with no water flow, was reduced by one-half with a water flow of 30 $gal/min/ft^2$.

## B42 Aeration Tower Sampling Points

By sampling at various points, one could consider the rate-loss in three ways: 1) from the whole tower as a unit; 2) from the spray head section alone; and 3) from the splash bar section alone. By sampling and determining the concentration of organics of the starting water in the first holding tank ($T_1$) and in the second holding tank ($T_2$) after passage through the tower we obtain the aeration loss from a series of whole tower passes. One whole tower being composed of the spray head section loss (0.5 ft. of the overall tower length of 9.5 ft.) and the splash bar section tower loss (9 ft. of the total 9.5 ft.). The approximate retention time of water in the whole tower was three seconds. By sampling after the spray head we could determine the loss on each pass due to the spray head section.

By sampling at the 4 ft. or 8 ft. sampling points or in the holding tank (equivalent to 9 ft. of splash bar section) we could determine the loss due to the splash bar section only.

By knowing the loss in each of the two sections we could, in effect, study the effect of any splash bar tower length preceded by only one spray head section.

## B43 Rate-Loss Data for Test 1, 2 and 3

In this section of the report three separate tower tests, Tests 1, 2 and 3, are evaluated. The test data are given in Table 37. In Table 37, Test 1, the nine compounds listed were all spiked as a group into finished water. In Tests 2 and 3, vinyl chloride and benzene were spiked

# TABLE 37

## RATE-LOSS DATA FROM AERATION TOWER (TEST 1,2 and 3)

SH = Spray Head

| | Test 2 | Test 1 | | | | | | | | | | | | | | | | | Test 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
| Initial Conc. (To) in $T_1$ | 112<br>108 | | | 81.9<br>79.5 | 88.0<br>67.5 | 122.1<br>120.1 | | | 107.5<br>103.4 | 74.2<br>69.1 | 157.7<br>151.6 | 139.2<br>139.5 | 195.1<br>202.0 | | 222.6<br>251.7 | | | | |
| ave. | 110 | | | 80.7 | 77.7 | 121 | | | 105.2 | 71.7 | 154.7 | 139.4 | 198.7 | | 237.2 | | | | 114.7 |
| $SH_1$ | | | | 67.1<br>57.9 | 71.6<br>55.3 | 102.6<br>95.1 | | | -<br>65.5 | 57.5<br>48.3 | 139.1<br>125.8 | 114.8<br>104.6 | 182<br>179.3 | | 196.1<br>231.3 | | | | |
| ave. | | | | 62.5 | 63.5 | 99 | | | 65.5 | 52.9 | 132.5 | 109.7 | 180.7 | | 213.7 | | | | |
| Conc. in $T_2$ after one tower pass | 17<br>11 | | | 10.7<br>16.3 | 19.4<br>17 | 25.6<br>28.8 | | | 6.6<br>10 | 7.6<br>8.7 | 53<br>47.1 | 18.5<br>11 | 69.3<br>67.2 | | 125.9<br>145.5 | | | | |
| ave. | 14 | | | 13.5 | 18.2 | 29.2 | | | 8.3 | 8.2 | 50.1 | 14.8 | 68.3 | | 135.2 | | | | 17.5 |
| $SH_2$ | | | | 10.6<br>11.5 | 13.5<br>15.1 | 23.7<br>25.9 | | | 6.5<br>6.5 | 6.8<br>7.6 | 42.5<br>45.3 | 10<br>10.4 | 75.5<br>80.8 | | 130.1<br>141.5 | | | | |
| ave. | | | | 11.1 | 14.3 | 24.8 | | | 6.5 | 7.2 | 43.9 | 10.2 | 78.2 | | 135.8 | | | | |
| Conc. in $T_1$ after 2 tower passes | 2.3<br>1.9 | | | 4.9<br>5.8 | 6.4<br>6.8 | 14.4<br>13.7 | | | 3.6<br>3.3 | 3.6<br>3.2 | 21.9<br>21.5 | 5.3<br>5.2 | 44<br>51 | | 46.3<br>140.2 | | | | |
| ave. | 2.1 | | | 5.4 | 6.6 | 16 | | | 3.45 | 3.4 | 21.7 | 5.3 | 47.5 | | 93.3 | | | | 9.1 |

(Continued)

## TABLE 37 (CONTINUED)

| | | Test 2 | Test 1 | | | | | | | | | | | | | | | | | Test 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
| $SH_3$ | | | | | 3.8<br>3.7 | 3<br>4.9 | 9.8<br>9.5 | | | 2<br>2.1 | 2.1<br>2.3 | 16.1<br>17.6 | 3.1<br>3.7 | 39.7<br>40.4 | | 78.7<br>71.8 | | | | |
| | ave. | | | | 3.8 | 4 | 9.7 | | | 2.1 | 2.2 | 16.9 | 3.4 | 40.1 | | 75.3 | | | | |
| Conc. in $T_2$ after 3 tower passes | | 0.21<br>0.13 | | | 1.3<br>1.3 | 1.6<br>2 | 5.9<br>4.5 | | | 0.8<br>0.5 | 0.5<br>0.7 | 7.8<br>8 | 1.5<br>1.2 | 25.9<br>22.4 | | 57.6<br>49.6 | | | | |
| | ave. | 0.17 | | | 1.3 | 1.8 | 5.2 | | | 0.65 | 0.6 | 7.9 | 1.4 | 24.2 | | 53.6 | | | | 3.14 |
| $SH_4$ | | | | | 0.8<br>1.4 | 1.3<br>1.5 | 3.6<br>4.2 | | | 0.3<br>0.2 | 0.4<br>0.3 | 6.1<br>6.3 | 0.8<br>0.7 | 18.9<br>14.5 | | 44.1<br>32.0 | | | | |
| | ave. | | | | 1.1 | 1.4 | 3.9 | | | 0.25 | 0.35 | 6.2 | 0.8 | 16.7 | | 38.0 | | | | |
| Conc. in $T_1$ after 4 tower passes | | nil<br>nil | | | 0.3<br>0.5 | 0.4<br>0.7 | 1.3<br>2 | | | 0.11<br>0.07 | 0.2<br>0.3 | 2.7<br>3.6 | 0.32<br>0.4 | 7.6<br>8.6 | | 18.5<br>20.3 | | | | |
| | ave. | nil | | | 0.4 | 0.6 | 1.7 | | | 0.09 | 0.25 | 3.2 | 0.36 | 8.1 | | 19.4 | | | | |
| $SH_5$ | | | | | 0.07<br>0.1 | 0.29<br>0.49 | 1.4<br>- | | | 0.09<br>0.08 | 0.1<br>0.1 | 2.2<br>2.3 | 0.28<br>0.2 | 7.5<br>6.7 | | 17.7<br>16.6 | | | | |
| | ave. | | | | 0.09 | 0.39 | 1.4 | | | 0.08 | 0.1 | 2.25 | 0.24 | 7.1 | | 17.2 | | | | |
| Conc. in $T_2$ after 5 tower passes | | nil<br>nil | | | 0.06<br>0.14 | 0.12<br>0.12 | 0.9<br>- | | | 0.04<br>0.02 | 0.05<br>0.06 | 1.2<br>1.25 | 0.08<br>0.08 | 3.9<br>3.9 | | 11.4<br>11.1 | | | | |
| | ave. | nil | | | 0.1 | 0.12 | 0.9 | | | 0.03 | 0.06 | 1.25 | 0.08 | 3.9 | | 11.25 | | | | |

separately. No forced air was used, and the water flow rate was 30 gal/min/ft$^2$.

The linear rate-loss plots (log concentration against whole tower passes) for the data in Table 37 for Tests 1 and 2 shown in Figures 50 and 51. As with beaker study data, it is apparent that a plot of log concentration against time (in this case one whole tower pass equals three seconds time) is linear. Expressed another way, the rate-loss per whole tower pass is independent of initial concentration.

In Test 1, 2 and 3, Table 37, sampling was done first in the holding tanks where the compounds were initially spiked. In Table 37, this sampling print was labled "initial concentration in $T_O$, $T_O$ for holding tank 0. The second sampling point, during the first tower pass, was made after the spray head section; labeled $SH_1$, in Table 37. The next sampling point, labeled $T_1$, gives the concentration in the holding tank receiving the water passed through the whole tower on the first pass, which is also the initial concentration of water ready to begin the second whole tower pass. By this sampling procedure, one can determine the rate-loss in the spray head section above (0.5 ft. of the 9.5 whole tower), in the splash bar section above (9 ft. of the whole tower), or in the whole tower itself as a single unit.

Since the rate-loss was constant for whole tower passes in series (rate-loss independent of initial concentration) this fact pertains to individual aeration systems making up the whole tower system, e.g. the spray head section alone and the splash bar section alone. From Table 37, the spray head sampling point data can be plotted separately. This has been done for chloroform in Figure 50 and carbon tetrachloride in Figure 51. The method of plotting compares the rate-loss in the spray head section of the tower, 0.5 ft., to the rate-loss of the whole tower, 9.5 ft. This was done by taking the initial concentration of chloroform, 121 μg/L, as the starting point on the "Y" axis. The second point, $SH_1$, in Table 37, 99 μg/L, was then plotted at the approximate 0.5 ft. coordinate on the "X" axis (1 whole tower pass unit on the "X"-axis equals 9.5 ft. of whole tower. Therefore, 0.5 ft. of spray head section is slightly more than one half of a single 1/10 division on the "X"-axis). A straight line was then drawn between these first 2 points and extended far enough, so the concentration in $T_1$ (the initial concentration entering the second spray head section pass) could be plotted on the extention. $SH_2$ was then plotted and a straight line drawn between $T_1$ and $SH_2$. As shown in Figure 50, for chloroform, the rate-loss in the spray head section was again independent of concentration. Also note, that on a per foot basis, the rate-dose was much greater for the spray head section than for the whole tower (later in the report some data will be plotted showing the rateloss in the splash bar section alone). From Figure 50, if an aeration system was made up of a series of spray head sections alone such that the total system was 9.5 ft. long, the final concentration of chloroform would be approximately 2 μg/L starting with an inital concentration of 121 μg/L, a reduction of approximately 98 percent, compared to a reduction of 65 percent for the 9.5 ft. of a whole tower pass.

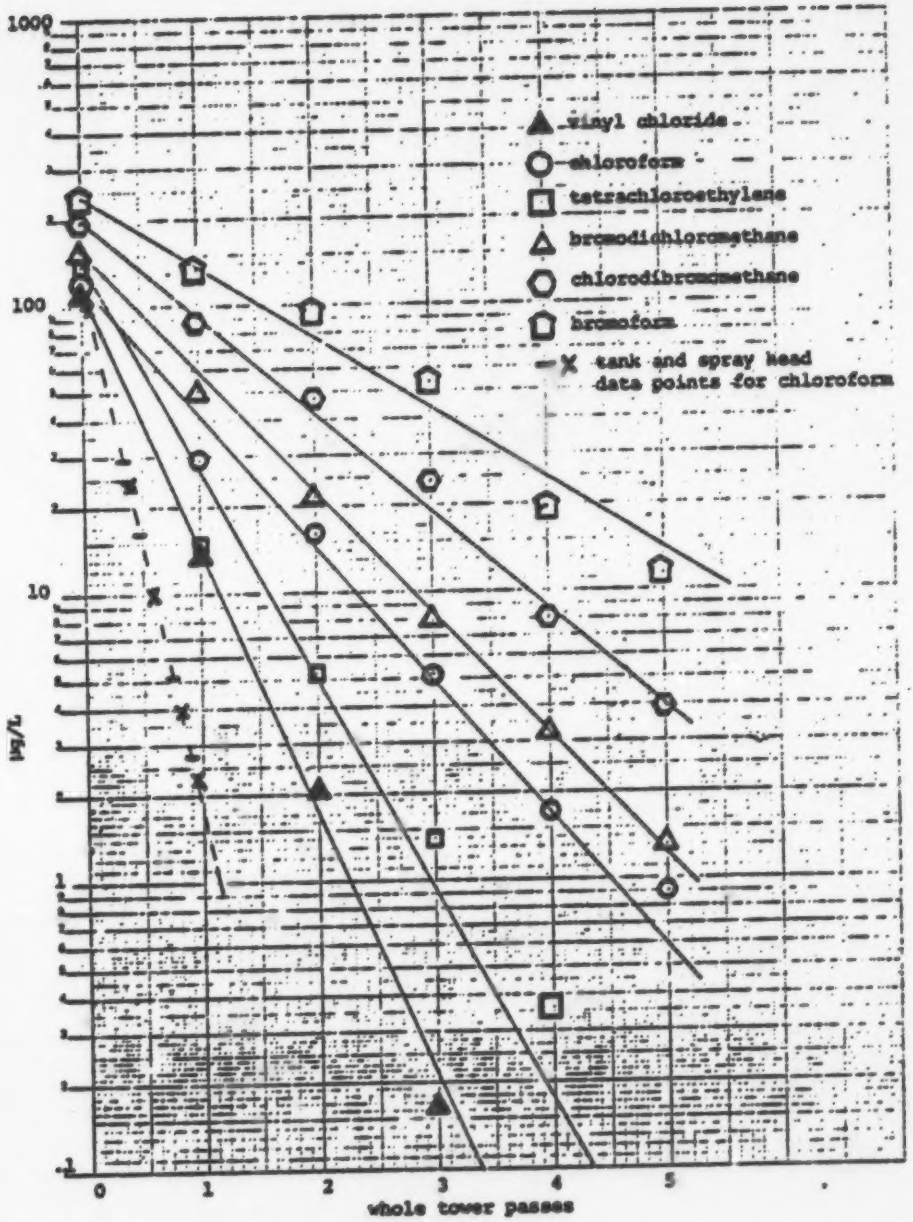


Figure 50 Rate-loss data from aeration tower (Tests 1 and 2).

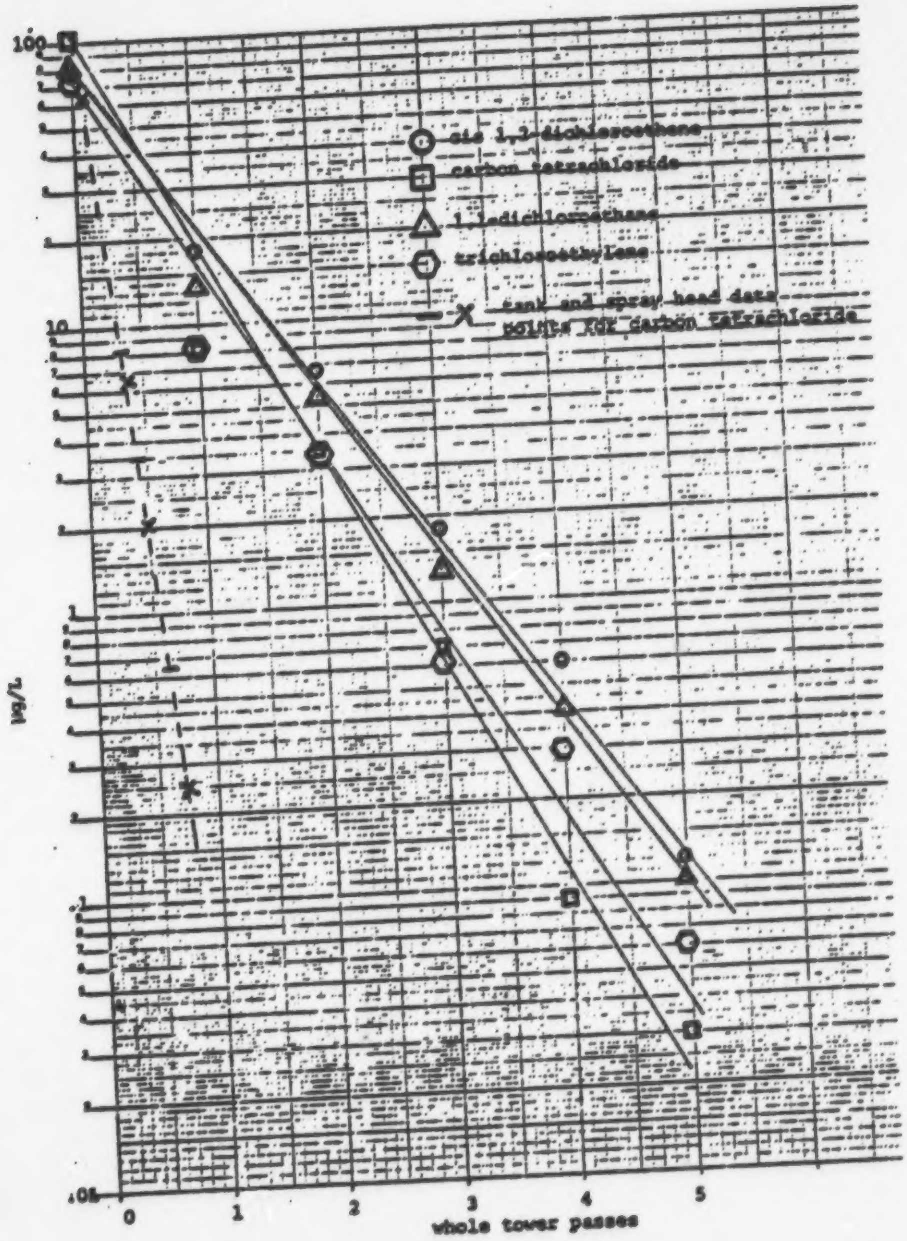


Figure 51 Rate-loss data from aeration tower (Test 1).

### B44 Plot of $H_{iPC}$ versus Slopes (Tests 1 and 2)

Using the slope equation (4), the slopes in Table 38, were calculated. The slopes for the compounds in Test 1 and 2 are plotted against $H_{iPC}$ in Figure 53. As with the beaker study data, these slopes fall near a straight line. In this case, even the bromoform datum point falls on this line. Liss and Slater (Ref. 18) show that the overall mass transfer coefficient across the interface is made up of two individual film mass transfer coefficents:

$$\frac{1}{K_{iOL}} = \frac{1}{K_{iL}} + \frac{1}{K_{iG}(\frac{H_i}{RT})} \tag{8}$$

where $K_{iOL}$ = overall mass transfer coefficient of compound i for a given interfacial system (m/hr)

$K_{iL}$ = mass transfer coefficient of compound i in the liquid film (m/hr)

$K_{iG}$ = mass transfer coefficient of compound i in the liquid film (m/hr)

R = the gas constant ($8.2\text{x}10^{-5}$) ($m^3$ atm g $mol^{-1}K^{-1}$)

t = absolute temperature ($^{o}K$)

$H_i$ = a Henry's Law constant (atm $m^3$/mol)

$$H_i = \frac{P_i}{C_{is}} \tag{9}$$

Apparently, as aeration conditions become more severe; e.g., interfacial area and air flow increases, $K_{iG}$, which is dependent on $H_i$, becomes a larger contribution to $K_{iOL}$.

Instead of plotting log $H_{iPC}$ versus slope, as in Figure 53, the percent of each compound removed by each whole tower pass can be plotted. The average percent removed for each compound whole tower pass, calculated from each linear line in Figures 50 and 51, is shown in Table 38. These values are plotted in Figure 54. Again, all points fall near a straight line. From such a plot the actual percent removed for any compound can be readily seen. Also, knowing the initial concentration of any compound, it is a simple matter to calculate the number of whole tower passes necessary to reduce the compound to any desired concentration, including essentially zero. For example, the chloroform initial concentration was 121 µg/L with 65 percent removal per whole tower pass, for 5 consecutive passes the concentrations per pass would be 42, 15, 5.2, 1.8 and 0.6 µg/L, respectively.

## TABLE 38

## CALCULATED RATE-LOSS SLOPE IN AERATION TOWER FOR TESTS 1, 2 AND 3

| | Test 2 | Test 1 | | | | | | | | | | | | | | | | Test 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_{lpc}$ | 4.2<br>5.3 | | | .24 | .29 | .15 | | | .97 | .48 | .039 | 1.2 | .043 | | .023 | | | .23 |
| | vinyl chloride | methylene chloride | trans 1,2-di-chloroethene | 1,1-di-chloroethane | cis 1,2-di-chloroethene | chloroform | 1,2-di-chloroethane | 1,1,1-tri-chloroethane | carbon tetra-chloride | trichloro-ethylene | bromodi-chloromethane | tetrachloro-ethylene | chlorodi-bromomethane | chlorobenzene | bromoform | p-chloro-toluene | p-dichloro-benzene | o-dichloro-benzene | benzene |
| slope | 2520 | | | 1564 | 1435 | 1300 | | | 1980 | 1733 | 1109 | 2079 | 934 | | 671 | | | | 1600 |
| % Removed per WTP * | 88 | | | 73 | 71 | 65 | | | 79 | 78 | 61 | 89 | 54 | | 44 | | | | 77 |

* WTP = whole tower pass

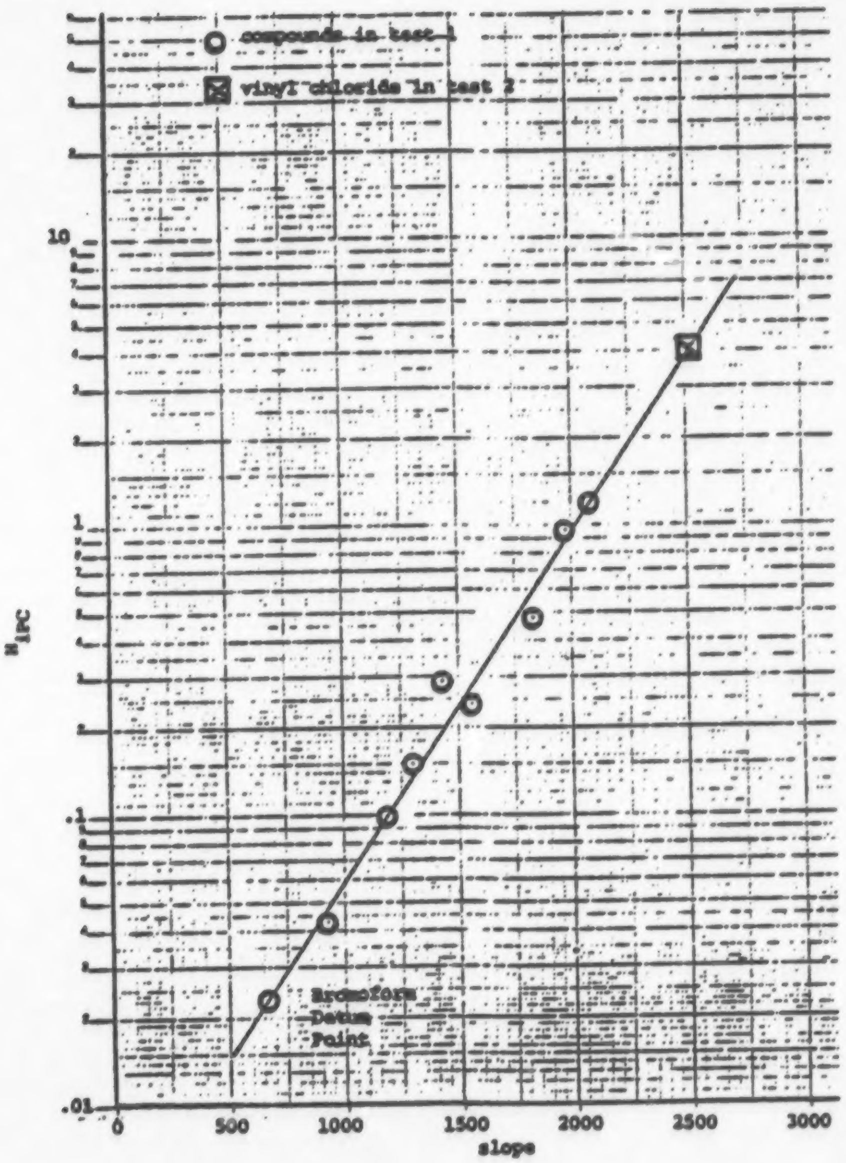


Figure 53 Plot of $H_{iPC}$ versus slope for whole tower pass data (Test 1 and 2).

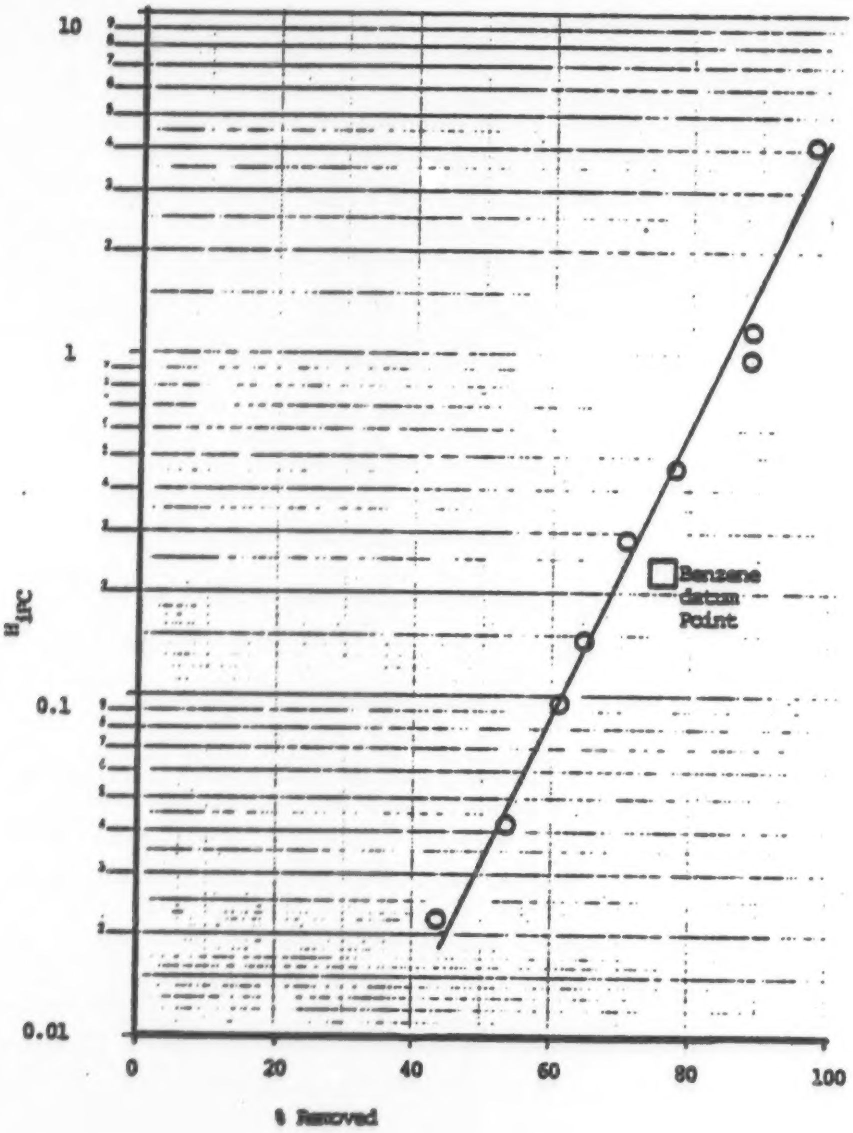


Figure 54 Plot of $H_{iPC}$ versus Percent removed values from Table 36 (Test 1 and 2)

### B45 $H_{iPC}$ of Vinyl Chloride

As discussed under the beaker study work, in Table 36, two $H_{iPC}$ values are given for vinyl chloride. These were reported by Dilling (Ref. 23) and are based on the uncertain solubility for vinyl chloride. When either reported $H_{iPC}$ value was used, vinyl chloride rate-loss data points obtained in the aeration tower did not fall on the straight line in Figure 54. After many very carefully controlled vinyl chloride tower tests, obtaining the same experimental results, it was concluded that either vinyl chloride, perhaps being a gas at our operating temperature does not fit into the family of other compounds falling on the straight line, or the reported values of $H_{iPC}$ were both in error. If the latter were true, by positioning the vinyl chloride datum point on the straight line at the appropriate rate-loss value, one could read the experimental $H_{iPC}$ value for vinyl chloride in Figure 54. The value appears to be 4.2. This compares quite closely with the 5.2 value found by the same method in the beaker study work. The two values, 4.2 and 5.2, are close, because only a slight error in reading the half life from the best-fit straight line log concentration versus time plot makes a significant difference in the calculated value.

### B46 Predicting Benzene Rate-Loss

As found with the beaker study work, if for any given aeration tower one experimentally measured the slope or percent removal for two compounds, separated by a meaningful distance, one should be able to construct the straight line as shown in Figure 54. Then, knowing the $H_{iPC}$ value for any other compound in a family of compounds, one should be able to predict its percent removal in the same aeration tower. To test this point, finished water was spiked with benzene. The results are reported in Table 36, Test #3, and plotted in Figure 55, indicating approximately an average reduction of 77 percent per whole tower pass. This datum point, 77 percent reduction, was plotted in Figure 54, versus the $H_{iPC}$ value of 0.23 for benzene. This single datum point falls close enough to the straight line to indicated that benzene may fit into the family of compounds whose slopes or percent reduction falls near the straight line. It is probable that most highly volatile organics of concern in drinking water, and perhaps many others which are not reactive with water, and whose $H_{iPC}$ values lie above 0.023, can be included in this family of compounds. For $H_{iPC}$ values less than this range, a straight line relationship with a different slope may still exist for other specific families of compounds.

### B47 Effect of Water Flow Rate on Rate-Loss in an Aeration Tower

In Tests 4, 5 and 6, data shown in Tables 39, 40 and 41, water was spiked with two concentration ranges of compounds, a high level and a

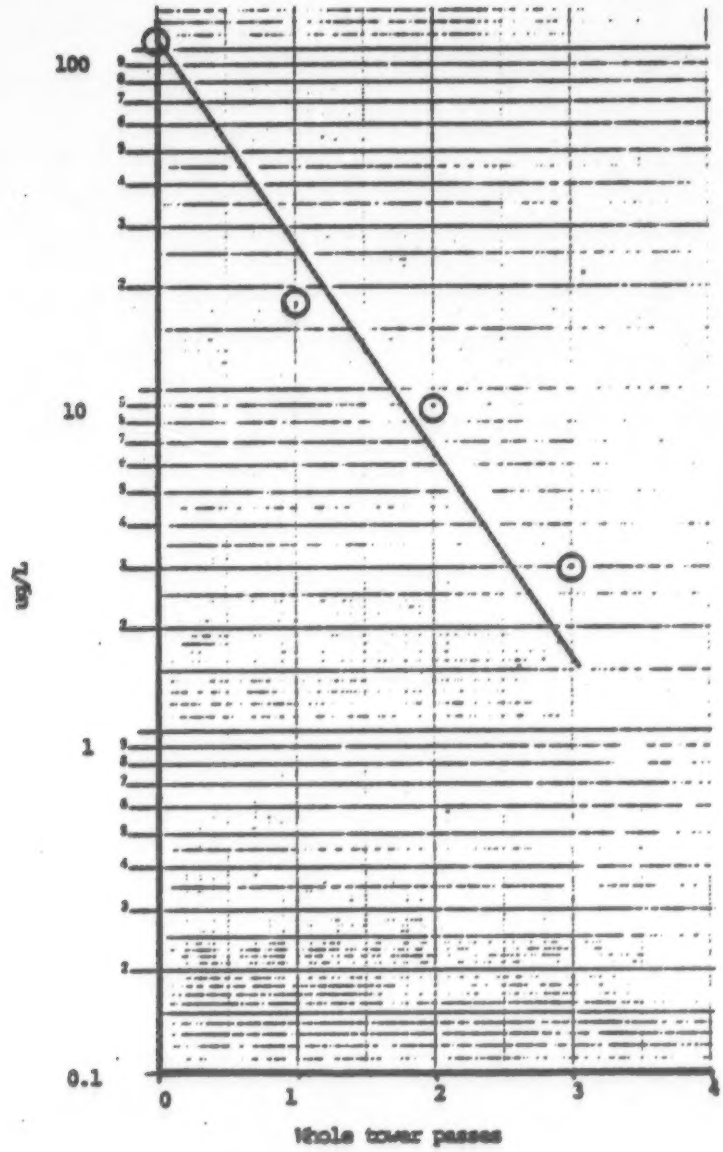


Figure 55 Benzene rate-loss from aeration tower (Test #3)

## TABLE 39

## RATE-LOSS DATA FROM AERATION TOWER AT VARYING WATER FLOW RATES (TEST 4)

Water Flow Rate 3 gal/min/ft$^2$ μg/L

| | | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TO | OS Low range | 63.4<br>55.8 | 5.7<br>5.1 | 3.4<br>2.8 | | 85.1<br>80.3 | 897<br>865 | | | | 5.3<br>4.7 | 943<br>929 | 0.52<br>0.48 | 351<br>333 | 16.8<br>16.2 | 41<br>37 | | 8.4<br>7.6 | 6.4<br>5.6 | |
| | ave. | 59.6 | 5.4 | 3.1 | | 82.7 | 881 | | | | 5 | 936 | 0.5 | 342 | 16.5 | 39 | | 8 | 6 | |
| | SH | 9.7<br>6.3 | 1.7<br>2 | 1.1<br>1.3 | | 27.9<br>44.2 | 630<br>570 | | | | 1.3<br>2.3 | 651<br>626 | 0.1<br>0.2 | 126<br>160 | 1.2<br>1.0 | 15.6<br>18.5 | | 4<br>2.7 | 3.3<br>- | |
| | ave. | 8 | 1.85 | 1.2 | | 36.1 | 600 | | | | 1.8 | 640 | 0.15 | 143 | 1.1 | 17.2 | | 3.35 | 3.3 | |
| | 4 feet | 0.28<br>nil | 0.9<br>0.8 | 0.2<br>nil | | 7.4<br>8.2 | 121<br>109 | | | | 0.2<br>0.1 | 118<br>125 | nil | 54<br>53 | 0.2<br>0.4 | 7.6<br>8.8 | | 0.8<br>nil | 0.8<br>nil | |
| | ave. | 0.14 | 0.85 | 0.1 | | 7.4 | 115 | | | | 0.15 | 121.5 | nil | 53.5 | 0.3 | 8.2 | | 0.4 | 0.4 | |
| | 8 feet | nil | 0.5<br>0.4 | nil | | 1<br>1.5 | 45<br>37 | | | | 0.3<br>nil | 56<br>40 | nil | 16.4<br>25 | nil | 7.9<br>5.5 | | nil | nil | |
| | ave. | nil | 0.45 | nil | | 1.25 | 41 | | | | 0.15 | 48 | nil | 21.2 | nil | 6.7 | | nil | nil | |
| % Removed (8 feet) | | 100 | 92 | 100 | | 98 | 95 | | | | 97 | 95 | | 94 | 100 | 83 | | 100 | 100 | |
| % Removed (WTP) | | 100 | | | | 100 | 98 | | | | | 97 | | 95 | | 84 | | | | |

(Continued)

To = starting tank
SH = Spray head
WTP = whole tower pass
OS = Original Spike Concentration

# TABLE 39 CONTINUED

Water Flow Rate 3 gal/min/ft$^2$ µg/L

| To | | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | m/p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| OS | high<br>range | | 19.9<br>18.7 | 43.1<br>35.3 | | 150<br>136 | 1667<br>1733 | | | | 14.[illegible]<br>15.8 | 2251<br>2165 | 21.2<br>16.8 | 713<br>677 | 43<br>39 | 93<br>87 | | | | |
| | ave. | | 19.3 | 39.2 | | 143 | 1700 | | | | 15 | 2208 | 19 | 695 | 41 | 90 | | | | |
| SH | | | 3.2<br>3.8 | 5.7<br>6.1 | | 74.5<br>82 | 1344<br>1448 | | | | 4.8<br>6.2 | 1675<br>1448 | 0.2<br>1.7 | 544<br>548 | 2.2<br>1.6 | 42<br>46 | | | | |
| | ave. | | 3.6 | 5.9 | | 78.3 | 1396 | | | | 5.5 | 1562 | 0.95 | 546 | 2 | 44 | | | | |
| 4 feet | | | -<br>1.7 | nil<br>0.5 | | 8.3<br>12.6 | 241<br>219 | | | | 0.6<br>1.3 | 385<br>297 | 0.1<br>- | 216<br>170 | 0.1<br>0.1 | 27<br>23 | | | | |
| | ave. | | 1.7 | 0.25 | | 10.5 | 230 | | | | 0.95 | 291 | 0.1 | 193 | 0.1 | 25 | | | | |
| 8 feet | | | 0.6<br>0.6 | nil | | 4.1<br>2.6 | 86<br>76 | | | | 0.2<br>0.1 | 105<br>100 | -<br>1.4 | 69<br>75 | nil | 18.4<br>15.6 | | | | |
| | ave. | | 0.6 | nil | | 3.4 | 81 | | | | 0.15 | 103 | 1.4 | 72 | nil | 17 | | | | |
| % Removed (8 feet) | | | 97 | 100 | | 98 | 95 | | | | 99 | 95 | 93 | 88 | 100 | 81 | | | | |
| % Removed (WTP) | | | | | | 99 | 97 | | | | | 93 | | 92 | | 86 | | | | |

## TABLE 40

## RATE-LOSS DATA FROM AERATION TOWER AT VARYING WATER FLOW RATES (TE-T 5)

μg/L Water flow rate 15 gal/min/ft²

| | vinyl chloride | methylene chloride | trans 1,2-dichloroethylene | 1,1-dichloroethane | cis 1,2-dichloroethane | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SW | 7.1<br>10.5 | 2.9<br>4 | 1.6<br>nil | | 45.3<br>52.8 | 469<br>526 | | | | 1.5<br>1.2 | 599<br>720 | 0.5<br>0.2 | 206<br>176 | 4.3<br>4.9 | 21.2<br>27.5 | | | | |
| ave. | 8.6 | 3.5 | 0.8 | | 49.1 | 503 | | | | 1.35 | 660 | 0.35 | 193 | 4.9 | 24.4 | | | | |
| 4 feet | 0.19<br>– | 1.1<br>– | 0.4<br>0.2 | | 15.2<br>15.6 | 192<br>190 | | | | 0.5<br>0.3 | 279<br>246 | nil | 101<br>0.2 | nil<br>0.2 | 14.0<br>15.8 | | | | |
| ave. | 0.19 | 1.1 | 0.3 | | 15.4 | 191 | | | | 0.4 | 263 | nil | 101 | 0.1 | 14.4 | | | | |
| 8 feet | nil | 0.6 | nil | | 4.8<br>6.6 | 167<br>96 | | | | 0.4<br>nil | –<br>167 | nil | 38<br>65 | 0.03<br>nil | 11<br>8.6 | | | | |
| ave. | nil | 0.6 | nil | | 5.7 | 132 | | | | 0.2 | 167 | nil | 52 | 0.015 | 9.9 | | | | |
| % Removed (8 feet) | 100 | 85 | 100 | | 93 | 85 | | | | 96 | 81 | 100 | 85 | 100 | 75 | | | | |
| % Removed (WTP) | 100 | | | | 95 | 90 | | | | | 88 | | 84 | | 76 | | | | |
| SW | | 7.7<br>7 | 8.5<br>6 | | 79<br>84 | 1051<br>1312 | | | | 6.1<br>6 | 1318<br>1677 | 1.4<br>3 | 494<br>632 | 2.7<br>2.2 | 86.3<br>69 | | | | |
| ave. | | 7.4 | 7.3 | | 81.5 | 1182 | | | | 6.05 | 1436 | 2.2 | 563 | 2.45 | 77.7 | | | | |
| 4 feet | | 4.2<br>3.9 | 1.2<br>nil | | 32<br>25.8 | 476-<br>595 | | | | 0.8<br>2 | 650<br>642 | 0.9<br>0.3 | 286<br>278 | 1.2<br>0.9 | 43.2<br>36 | | | | |
| ave. | | 4.15 | 0.6 | | 28.9 | 536 | | | | 1.4 | 646 | 0.6 | 282 | 1.05 | 38.1 | | | | |
| 8 feet | | 2.9<br>2.6 | nil | | 8<br>9.6 | 246<br>292 | | | | 0.9<br>1.2 | 363<br>327 | 1.6<br>0.9 | 151<br>170 | nil<br>0.1 | 32<br>24 | | | | |
| ave. | | 2.3 | nil | | 8.8 | 269 | | | | 1.05 | 345 | 1.25 | 161 | 0.5 | 28 | | | | |
| % Removed (8 feet) | | 88 | 100 | | 94 | 84 | | | | 93 | 84 | 93 | 77 | 99 | 69 | | | | |
| % Removed (WTP) | | | | | 96 | 87 | | | | | 90 | | 91 | | 77 | | | | |

## TABLE 41

## RATE-LOSS DATA FROM AERATION TOWER AT VARYING WATER FLOW RATES (TEST 6)

μg/L Water flow rate 30 gal/min/ft$^2$

| | vinyl chloride | methylene chloride | trans 1,2-dichloroethylene | 1,1-dichloroethane | cis 1,2-dichloroethylene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | [illegible] | tetrachloroethylene | chlorobenzene | bromoform | chlorodibromomethane | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SH | 31.2<br>20.8 | 3.8<br>3.6 | 1.7<br>1.7 | | 57.7<br>51 | 554<br>535 | | | | 2.2<br>- | 677<br>661 | 0.1<br>0.2 | 3<br>3.1 | 28.7<br>31.5 | | | 3.7<br>- | 3.3<br>- | |
| ave. | 27 | 3.7 | 1.7 | | 54.3 | 545 | | | | 2.2 | 669 | 0.15 | 3.05 | 30.1 | | | 3.7 | 3.3 | |
| 4 foot | 13.5<br>8.5 | 2.5<br>- | 0.3<br>0.2 | | 32.3<br>27.9 | 226<br>283 | | | | 1.5<br>0.7 | 326<br>344 | -<br>nil | 0.4<br>3.7 | 20.6<br>21.4 | | | 0.4<br>- | 0.1<br>nil | |
| ave. | 11 | 2.5 | 0.25 | | 30.1 | 255 | | | | 1.1 | 335 | nil | 2.05 | 21 | | | 0.4 | 0.05 | |
| 8 feet | 3.4<br>4.1 | 1.9<br>- | nil | | 15.1<br>10.6 | 159<br>192 | | | | nil | 241<br>209 | nil | nil | 16<br>14.4 | | | nil | nil | |
| ave. | 3.75 | 1.9 | nil | | 13 | 176 | | | | nil | 225 | nil | nil | 15.2 | | | nil | nil | |
| % Removed (8 feet) | 94 | 65 | 100 | | 84 | 80 | | | | 100 | 76 | 100 | 100 | 61 | 58 | | | | |
| % Removed (WTP) | 95 | | | | 84 | 81 | | | | | 79 | | | 62 | 63 | | | | |
| SH | 8.5<br>8 | | 8.5<br>7.5 | | 87<br>97.8 | -<br>1293 | | | | 4.8<br>7.4 | 1322<br>1444 | 0.8<br>1.4 | 13.3<br>6.7 | 76.4<br>88.4 | | | | | |
| ave. | 8.25 | | 8 | | 92.4 | 1293 | | | | 6.1 | 1383 | 1.1 | 10 | 82.4 | | | | | |
| 4 feet | 6.8<br>- | | 0.2<br>nil | | 46.7<br>41.5 | 708<br>700 | | | | 4.1<br>- | 880<br>838 | 0.1<br>- | 1.8<br>2.2 | 52.4<br>60 | | | | | |
| ave. | 6.8 | | 0.1 | | 44.1 | 704 | | | | 4.1 | 859 | 0.1 | 2 | 56.2 | | | | | |
| 8 foot | 4.2<br>6.2 | | nil<br>1.5 | | 25.5<br>23.5 | 399<br>393 | | | | -<br>2.6 | 546<br>513 | -<br>1.4 | 0.2<br>nil | 48<br>40 | | | | | |
| ave. | 5.2 | | 0.75 | | 24.5 | 396 | | | | 2.6 | 530 | 1.4 | 0.1 | 44 | | | | | |
| % Removed (8 feet) | 73 | | 98 | | 81 | 77 | | | | 83 | 76 | 93 | 100 | 51 | 60 | | | | |
| % Removed (WTP) | | | | | 85 | 79 | | | | | 80 | | | 53 | 55 | | | | |

lower level. The rate-loss was measured with 3, 15 and 30 gal/min/ft$^2$ of water flow. One pass through the aeration tower was made, using no forced air. Samples were taken in the holding tanks, after the spray head, and after 4 and 8 ft. of splash bar tower. These data are plotted in Figures 56 thru 63 in such a way to show the rate-loss for all three aeration sections, 1) the spray head section, 2) the splash bar section and 3) the whole tower as a unit. The chloroform data from Tables 39, 40 and 41 are plotted in Figure 56. The X-axis scale is in feet (four graduations per foot). Below this X-axis scale, separate bench marks are shown representing 0.5 ft. of spray head and the 4 and 8 ft. of splash bar sections at 4.5 ft. and 8.5 ft. of wide tower length, and the whole tower length of 9.5 ft.. Above the X-axis side, starting at the 0.5 ft. bench scale mark, additional bench scale marks represent the 0, 4 and 8 ft. section of splash bar tower. The initial concentration for chloroform in the high spike run (1700 µg/L from Table 39) was plotted on the Y-axis coordinate as shown in Figure 56. The concentration after the spray head for this run was plotted on the 0.5 foot coordinate. A dashed line was then drawn between these first two points, representing the spray head loss. The concentrations at the four-foot and eight splash bar tower section was plotted on the 4.5 ft. and 8.5 ft. X-axis coordinate, respectively. A best-fit straight line was then drawn through the three plotted points, representing; the influent concentration to the splash bar section and the 4 and 8 ft. sampling points. The after-spray-head concentration of the low spiked run was then plotted on the best-fit line. The initial concentration in the low spiked run was then plotted 0.5 foot to the left of this point. The 4 and 8 ft. points were then plotted the appropriate X-axis distance (4 and 8 ft.) from the spray head point. The rate-loss concentration for the whole tower as a unit can be drawn by connecting points A and B, as shown by the heavy line A-B in Figure 56. The line was drawn from the initial concentration on the high spike run to the 9.5 ft. coordinate on the splash bar tower section straight line. In this series of tests varying the water raw rate, it should be pointed out that at the 3 gal/min/ft.$^2$ flow rate, the spray heads did not all operate, and more water passed through some than others. This probably affected the removal results for this low level water flow compared to the other two flow rates. Vinyl chloride was spiked only at one concentration. The percent of each compound removed after a whole tower pass is shown in Tables 39, 40 and 41. These values are plotted in Figure 64. The plots of log $H_{iPC}$ versus percent removal, again fall near a straight line for each water flow rate. The vinyl chloride data points being at or near 100 percent removal do not fit into the slope of the straight lines because the lines will approach 100 percent removed before the $H_{iPC}$ value for vinyl chloride is reached. It can be concluded that decreasing the rate of water flow does increase the rate-loss for all compounds studied. Probably, the main reason in lowering water flow in a given system would be to more extensively remove the lower $H_{iPC}$ compounds. To go beyond the relationship shown by the plotted data in Figure 64 would be difficult. One reason being that as the water flow rate was changed, a change also occured in the air flow rate. However, a rectanglar plot of the data in Figure 64 is shown in Figure 65. It is not suggested that the data are linear on such a plot. The data may approach linearity for compounds of higher $H_{iPC}$. However, the curves in

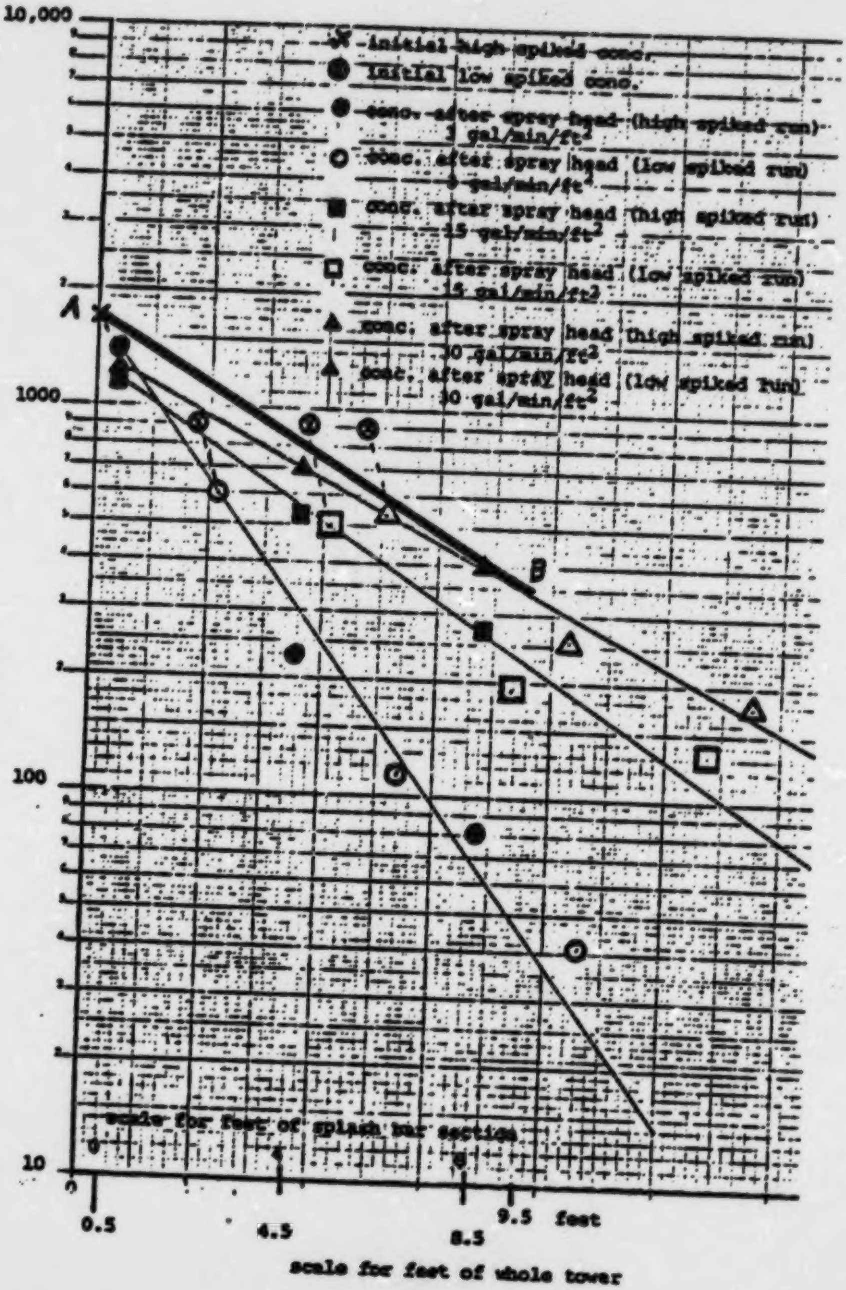


Figure 56 Chloroform rate-loss data obtained in aeration tower varying water flow rates (Test 4, 5 and 6)

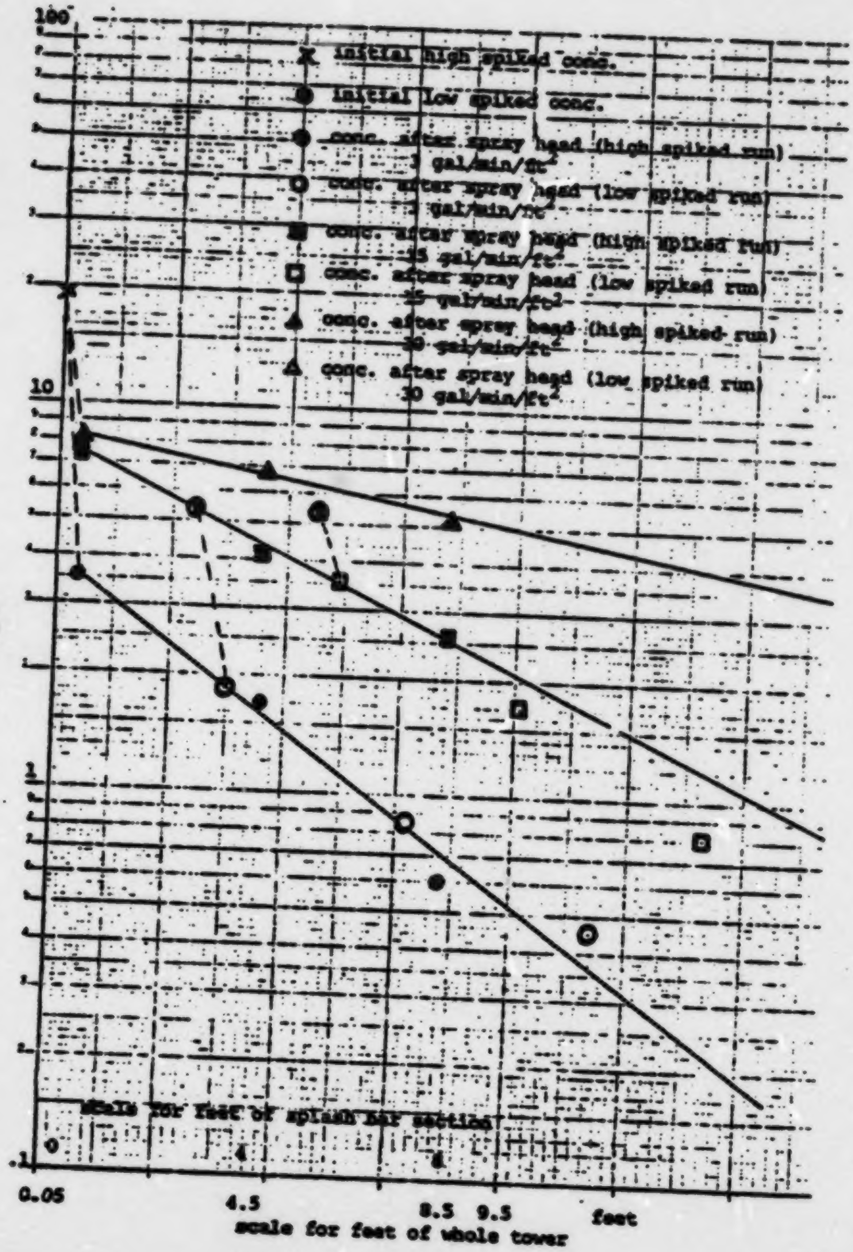


Figure 57 Methylene chloride rate-loss data obtained in aeration tower varying water flow rates (Tests 4, 5 and 6).

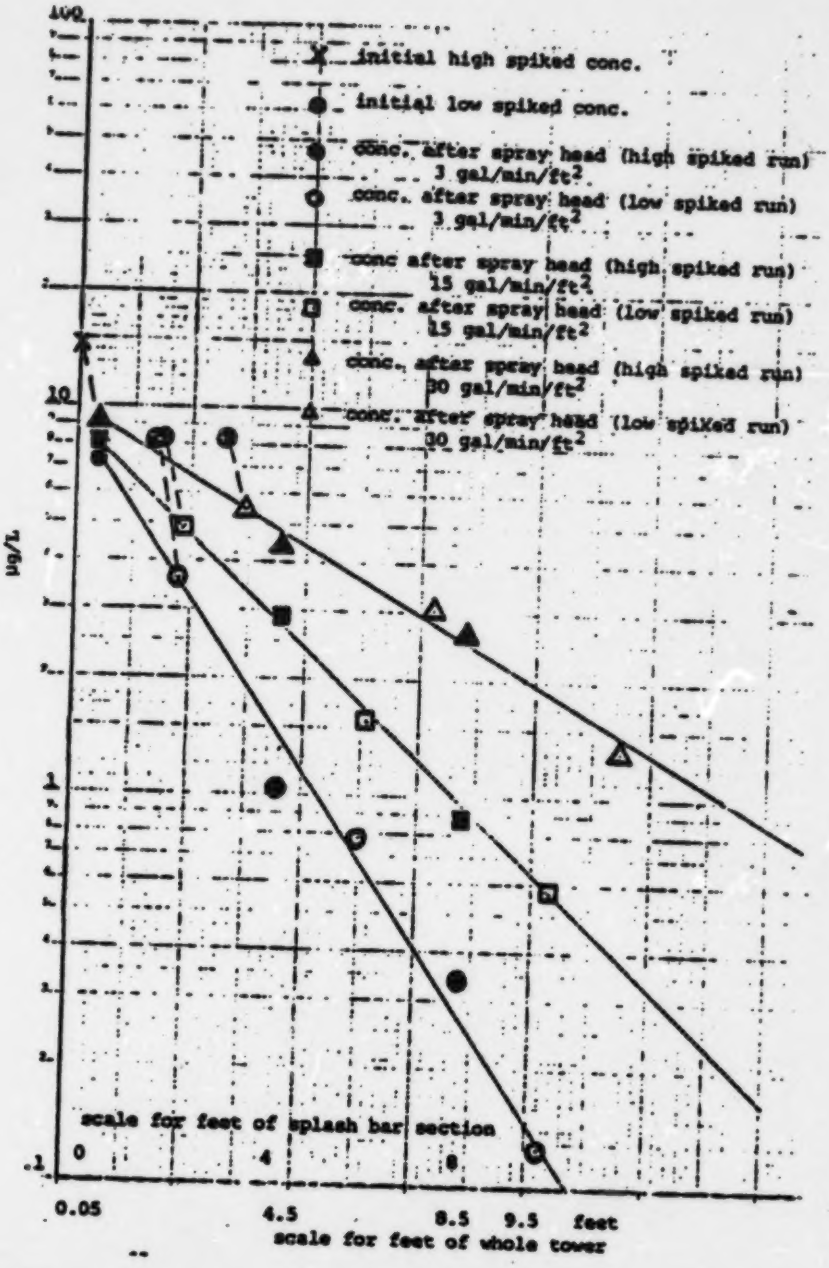


Figure 58 Cis 1,2-dichloroethene rate-loss data obtained in aeration tower varying water flow rate (Tests 4, 5 and 6).

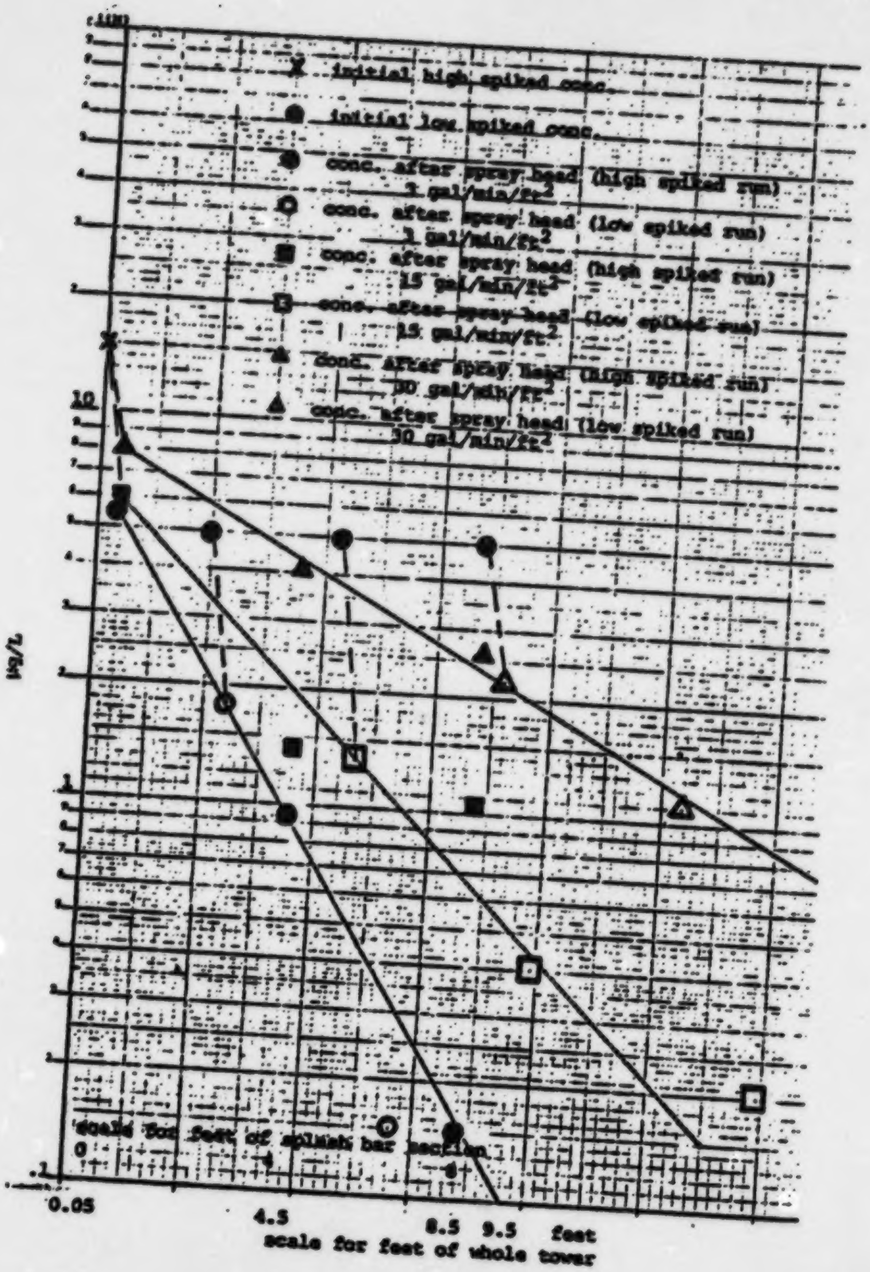


Figure 59 Trichloroethylene rate-loss data obtained in aeration tower varying water flow rate (Tests 4, 5 and 6).

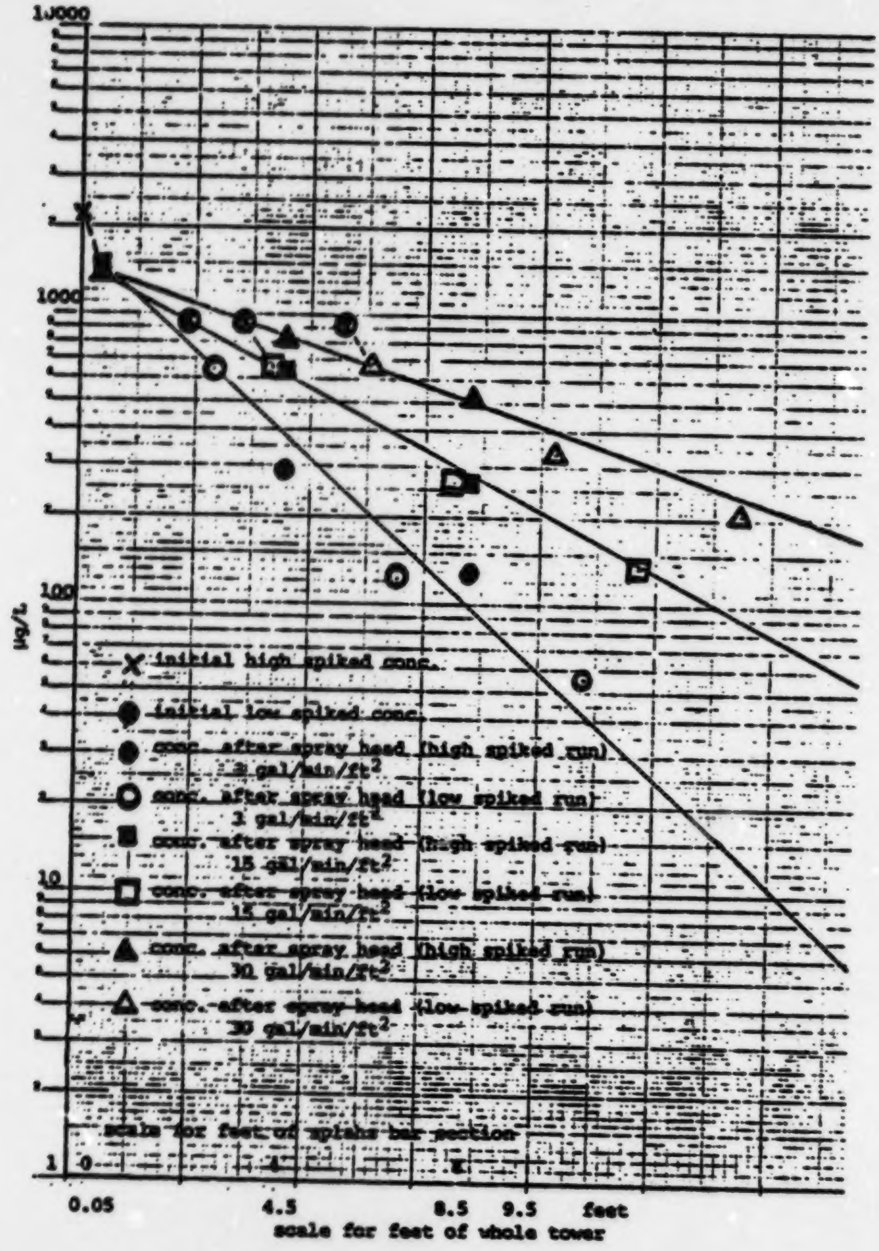


Figure 60 Bromodichloromethane rate-loss data obtained in aeration tower varying water flow rate (Tests 4, 5 and 6).

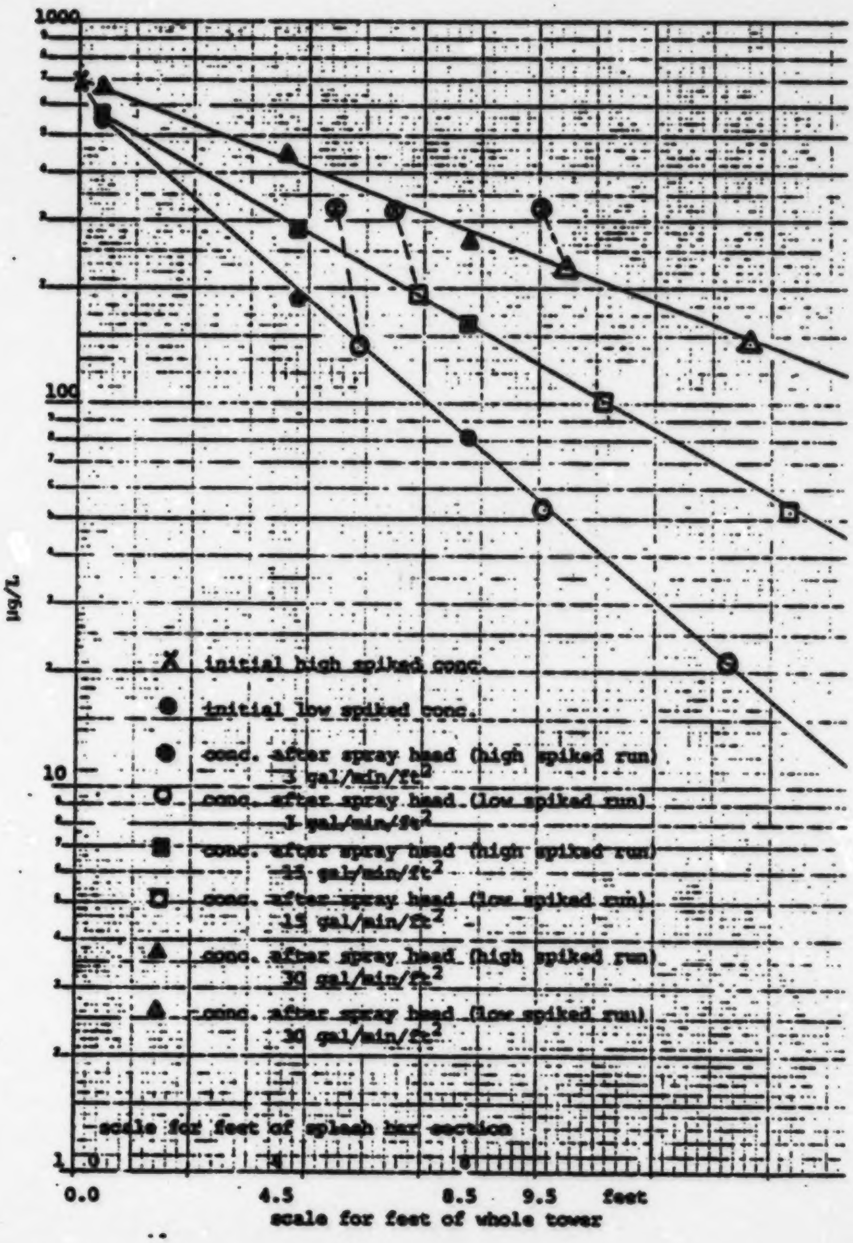


Figure 61 Chlorodibromomethane rate-loss data obtained in aeration tower varying water flow rate (Tests 4, 5 and 6)

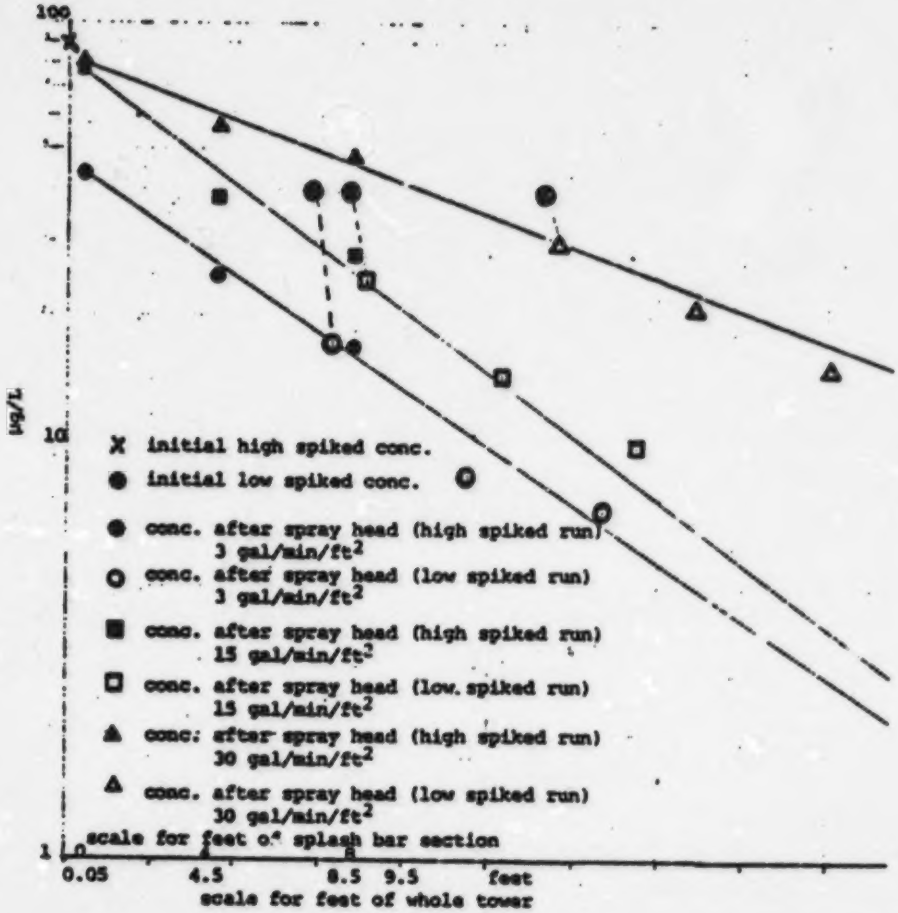


Figure 62 Bromoform rate-loss data obtained in aeration tower varying water flow rate (Tests 4, 5 and 6).

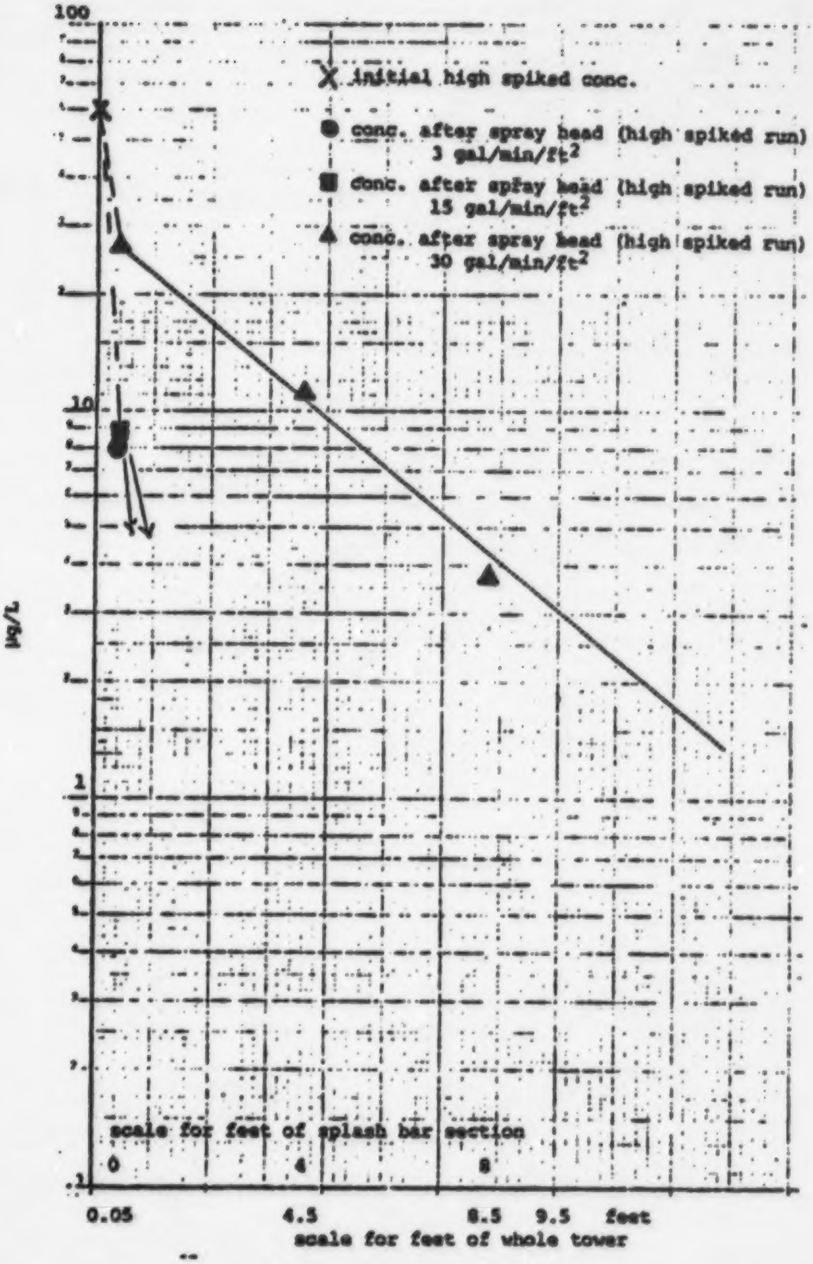


Figure 63 Vinyl chloride rate-loss data obtained from aeration tower varying water flow rate (Tests 4, 5 and 6).

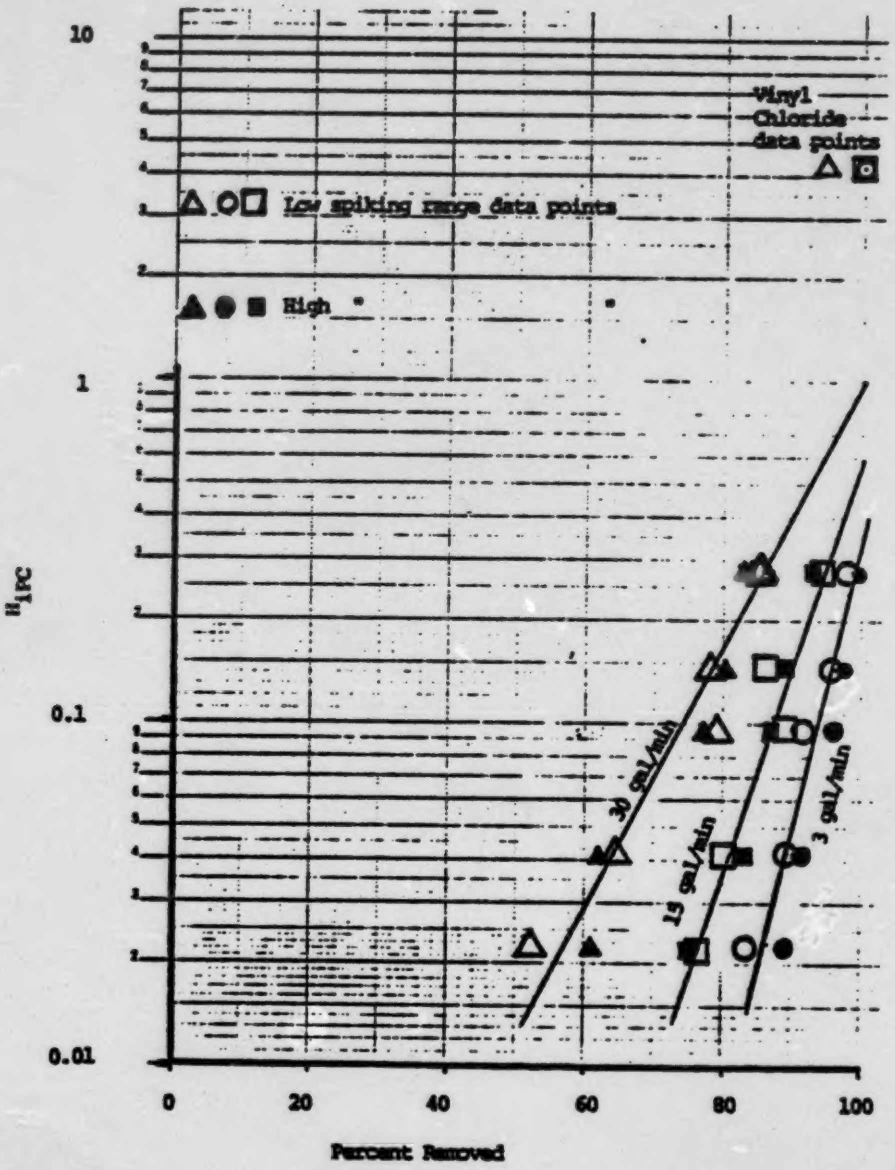


Figure 64 Rate-loss data from aeration tower (Tests 4, 5 and 6) varying water flow rates.

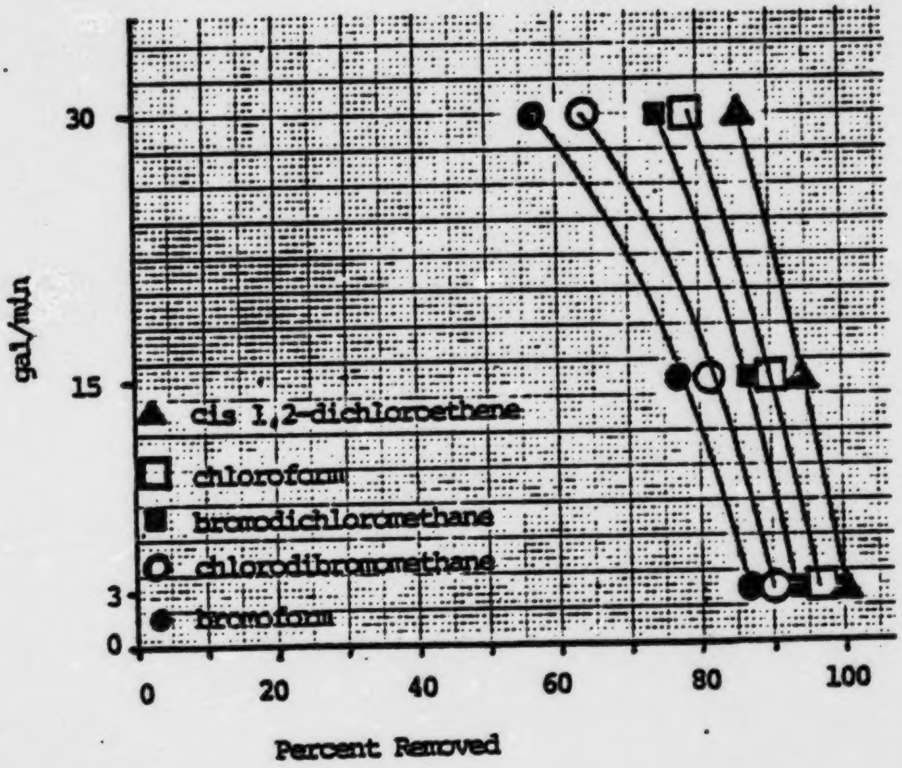


Figure 65 Rectangular plot of data from Figure 64

Figure 65 can aid in predicting the water flow rate necessary to achieve a given rate loss for the compounds shown and for compounds whose $H_{iPC}$ value is known.

### B48 Effect of Air Flow on Rate-Loss in an Aeration Tower

In Tests 7, 8 and 9 the effects of air flow on rate-loss at 30 gal/min/ft$^{2}$ of water flow was studied. Air flow was varied from no forced draft (natural chimney effect), to 100 and 225 ft$^{3}$/min/ft$^{2}$. Rate-loss data are presented in Tables 42, 43 and 44. The rate-loss plots for each compound are plotted in Figures 66 thru 70. From these plots, it is apparent that going from no forced draft to 100 ft$^{3}$/min a significant increase was achieved in rate-loss. However, going from 100 to 225 ft$^{3}$/min, the increase in rate-loss was lower than the first incremental increase. Since most of the resistance to evaporation of a compound from water is in the liquid phase (Mackay and Wolkoff, (Ref. 25), it is not surprising that the rate-loss is not directly proportional to increased air flow. One might expect something like an exponential decay in rate-loss benefits with increased air flow beyond a certain point. Rate-loss differences were noted when no forced air was used in the aeration tower due to the changes in natural draft which in turn was related to the cross wind velocity. It was estimated that on a calm day the natural draft was approximately one or two cubic feet per minute. On windy days it was estimated that gusts of natural draft up to 10 ft$^{3}$/min were experienced, but even on windy days the sustained natural draft was probably only 3 to 4 ft$^{3}$/min. The percent reduction in concentration for the major chemicals per whole tower pass is shown in Tables 42, 43 and 44. These data are plotted in Figure 71. It is apparent that once again for each aeration system, that data points fall near a straight line plot and increasing the air flow rate from no forced draft to 100 ft$^{3}$/min. resulted in a much larger increase in percent removal, than the increased air flow rate from 100 to 225 ft$^{3}$ min. The straight line values corresponding to a particular $H_{iPC}$ values are presented in a rectanglar plot in Figure 72. Once again, it shows the change is greater for the first incremental air flow increase. These curves allow some capability of predicting the air flow rate necessary to give given percent reduction of any compound.

### B49 Aeration Tower Length Versus Water and Air Flow Rates

Following the removal rate of chloroform as an example with an intermediate $H_{iPC}$ value, the merits of using increased tower length, decreased water flow rate or increased air flow rate to achieve any desired removal rate can be compared.

From Figure 49, 66 and 72, the chloroform removal rate with no forced air through the aeration-tower and with a water flow rate of 30 gal/min/ft$^{2}$, chloroform removal rates of 65, 78 and 67 percent were achieved, differences resulting from natural draft conditions on the particular test day. For

# TABLE 42

## RATE-LOSS DATA FOR ORGANICS IN AERATION TOWER VARYING AIR FLOW RATES (TEST 7)

Test 7  no forced draft -  µg/L.

|  | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | trichlorofluoromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fin. water Int. conc. | [illegible]<br>[illegible]<br>- | [illegible]<br>0.4<br>- | [illegible]<br>[illegible]<br>- | [illegible]<br>[illegible]<br>- | [illegible]<br>[illegible]<br>25.5 | 67.2<br>65.8<br>68.3 |  |  |  | [illegible]<br>[illegible]<br>0.11 | 88.3<br>82<br>76.9 | [illegible]<br>0.03<br>- | [illegible]<br>34<br>36.2 | [illegible]<br>1.6<br>1.5 | [illegible]<br>3.9<br>5.1 |  | 0.27<br>0.24<br>0.5 | [illegible]<br>[illegible]<br>0.1 |  |
| ave. | 6.25 | 0.405 | 0.53 | 0.5 | 23.4 | 67.1 |  |  |  | 0.19 | 82.4 | 0.1 | 35.2 | 1.3 | 4.3 |  | 0.34 | 0.19 |  |
| 1 tower pass | 0.03<br>0.02 | 0.2<br>nil | nil | nil | 6.9<br>6.1 | 20.3<br>-<br>- |  |  |  | nil | 32.5<br>30.5<br>- | nil | 22.3<br>[illegible]<br>22.0 | 0.1<br>0.10<br>0.1 | 2.9<br>3.4<br>- |  | 0.1<br>-<br>0.09 | 0.1<br>- |  |
| % removed ave. | 0.025 | 0.1 | nil | nil | 6.5<br>(72) | 20.3<br>(70) |  |  |  | nil | 31.5<br>(62) | nil | 22.1<br>(44) | 0.13 | 3.2<br>(26) |  | 0.095 | 0.1 |  |
| 2 | nil | nil | nil | nil | [illegible]<br>[illegible] | 7.1<br>-<br>- |  |  |  | nil | [illegible]<br>[illegible]<br>[illegible] | nil | [illegible]<br>[illegible]<br>3.6 | nil | [illegible]<br>0.63<br>- |  | nil | nil |  |
| % removed ave. | nil | nil | nil | nil | 1.9<br>(71) | 7.1<br>(65) |  |  |  | nil | 9.8<br>(69) | nil | 8.0<br>(64) | nil | 1.3<br>(59) |  | nil | nil |  |
| 3 | nil | nil | nil | nil | [illegible]<br>0.31 | 1.9<br>1.7<br>- |  |  |  | nil | [illegible]<br>3.0<br>- | nil | [illegible]<br>3.0<br>3.5 | nil | 0.61<br>[illegible]<br>- |  | nil | nil |  |
| % removed ave. | nil | nil | nil | nil | 0.35 | 1.8<br>(75) |  |  |  | nil | 2.5<br>(74) | nil | 3.6<br>(55) | nil | 0.63<br>(51) |  | nil | nil |  |
| 4 | nil | nil | nil | nil | nil<br>0.2 | -<br>-<br>- |  |  |  | nil | [illegible]<br>1.4<br>- | nil | [illegible]<br>2.6<br>2.4 | 0.1<br>nil<br>nil | [illegible]<br>0.33<br>- |  | nil | nil |  |
| ave. | nil | nil | nil | nil | 0.1 | - |  |  |  | nil | 1.7 | nil | 2.4 | trace | 0.325 |  | nil | nil |  |
| 5 | nil | nil | nil | nil | nil | nil<br>0.4<br>- |  |  |  | nil | 0.29<br>-<br>- | nil | 0.31<br>0.74<br>- | nil | 0.21<br>-<br>- |  | nil | nil |  |
| ave. | nil | nil | nil | nil | nil | 0.2 |  |  |  | nil | 0.29 | nil | 0.44 | nil | 0.21 |  | nil | nil |  |
| average % removed |  |  |  |  | 72 | 70 |  |  |  |  | 68 |  | 54 |  | 45 |  |  |  |  |

## TABLE 43

## RATE-LOSS DATA FOR ORGANICS IN AERATION TOWER VARYING AIR FLOW RATES (TEST 8)

Test 8 100 $ft^3/min/ft^3$ µg/L

|  | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethylene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 Tower Pass |  |  |  |  | 5.5<br>5.3 | 21.1<br>15.5 |  |  |  | 0.3<br>nil | 22.3<br>18.7 | nil<br>0.09 | 14.2<br>15.6 | -<br>- | 2.1<br>1.7 |  | 0.06<br>0.06 | 0.14<br>0.08 |  |
| 1/0 removed | - | - | - |  | 5.6<br>(76) | 18.3<br>(73) |  |  |  | 0.15 | 20.5<br>(75) | 0.05 | 14.9<br>(62) | - | 1.9<br>(56) |  | 0.06 | 0.11 |  |
| 2 |  |  |  |  | 1.8<br>1.0 | 7.1<br>3.7 |  |  |  | 0.04<br>nil | 7.3<br>6.3 | nil<br>0.02 | 6.5<br>4.3 | nil<br>0.15 | 0.55<br>0.67 |  | 0.08<br>nil | nil |  |
| 0/0 removed | - | - | - |  | 1.4<br>(75) | 3.4<br>(70) |  |  |  | 0.02 | 6.0<br>(67) | 0.01 | 5.4<br>(64) | 0.075 | 0.81<br>(57) |  | 0.04 | nil |  |
| 3 |  |  |  |  | 0.13<br>0.35 | 1.4<br>1.0 |  |  |  | nil | 0.9<br>2.1 | nil | 2.0<br>1.0 | nil | 0.32<br>0.22 |  | nil | nil |  |
| 0/0 removed | - | - | - |  | 0.24<br>(83) | 1.2<br>(78) |  |  |  | nil | 1.5<br>(78) | nil | 1.5<br>(72) | nil | 0.27<br>(67) |  | nil | nil |  |
| 4 |  |  |  |  | 0.12<br>0.02 | 0.6<br>nil |  |  |  | nil | 0.42<br>- | nil | 0.02<br>nil | nil | 0.10<br>0.1 |  | nil | nil |  |
| 0/0 removed | - | - | - |  | 0.07 | (75)<br>0.3 |  |  |  | nil | (73)<br>0.14 | nil | 0.02 | nil | 0.14 |  | nil | nil |  |
| 5 |  |  |  |  | nil | nil |  |  |  | nil | -<br>0.16 | nil | 0.2<br>nil | nil | 0.1<br>[illegible] |  | nil | nil |  |
|  | - | - | - |  | nil | nil |  |  |  | nil | 0.14 | nil | 0.2 | nil | 0.05 |  | nil | nil |  |
| average % removed |  |  |  |  | 78 | 74 |  |  |  | 73 |  |  | 66 |  | 60 |  |  |  |  |

## TABLE 44

## RATE-LOSS DATA FOR ORGANICS IN AERATION TOWER VARYING AIR FLOW RATE (TEST 9)

Test 9   325 ft³/min/ft²   µg/L

| | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 Tower Pass | nil | nil | nil | nil | 6.2<br>3.3 | 17.1<br>13.1 | | | | nil | 19.7<br>17.1 | nil | 10.9<br>12.2 | nil | 1.96<br>1.3 | | nil | nil | |
| % removed | nil | nil | nil | nil | 4.5<br>(81) | 15<br>(76) | | | | nil | 18.4<br>(78) | nil | 11.6<br>(70) | nil | 1.63<br>(62) | | nil | nil | |
| 2 | nil | nil | nil | nil | 1.8<br>0.4 | 5.1<br>3.5 | | | | nil | 4.5<br>7.9 | nil | 4.1<br>2.6 | nil | 0.63<br>1.08 | | nil | nil | |
| % removed | nil | nil | nil | nil | (76)<br>1.1 | (71)<br>4.3 | | | | nil | (86)<br>6.3 | nil | (71)<br>3.4 | nil | (48)<br>0.84 | | nil | nil | |
| 3 | nil | nil | nil | nil | 0.21<br>0.09 | 1.6<br>0.4 | | | | nil | -<br>1.93 | nil | 1.1<br>1.7 | nil | 0.34<br>0.46 | | nil | nil | |
| % removed | nil | nil | nil | nil | (86)<br>0.15 | (77)<br>1.0 | | | | nil | (69)<br>[illegible] | nil | (59)<br>1.4 | nil | (58)<br>0.35 | | nil | nil | |
| 4 | nil | nil | nil | nil | 0.1<br>nil | 0.3<br>0.01 | | | | nil | 0.61<br>0.05 | nil | 0.31<br>0.15 | nil | 0.18<br>0.06 | | nil | nil | |
| % removed | nil | nil | nil | nil | 0.05 | 0.18<br>(82) | | | | nil | 0.33<br>(83) | nil | 0.23<br>(84) | nil | 0.12 | | nil | nil | |
| 5 | nil | nil | nil | nil | nil | nil | | | | nil | 0.15<br>nil | nil | 0.135<br>- | nil | 0.05<br>- | | nil | nil | |
| | nil | nil | nil | nil | nil | nil | | | | nil | 0.03 | nil | 0.105 | nil | 0.05 | | nil | nil | |
| average % removed | | | | | 81 | 77 | | | | | 74 | | 70 | | 56 | | | | |

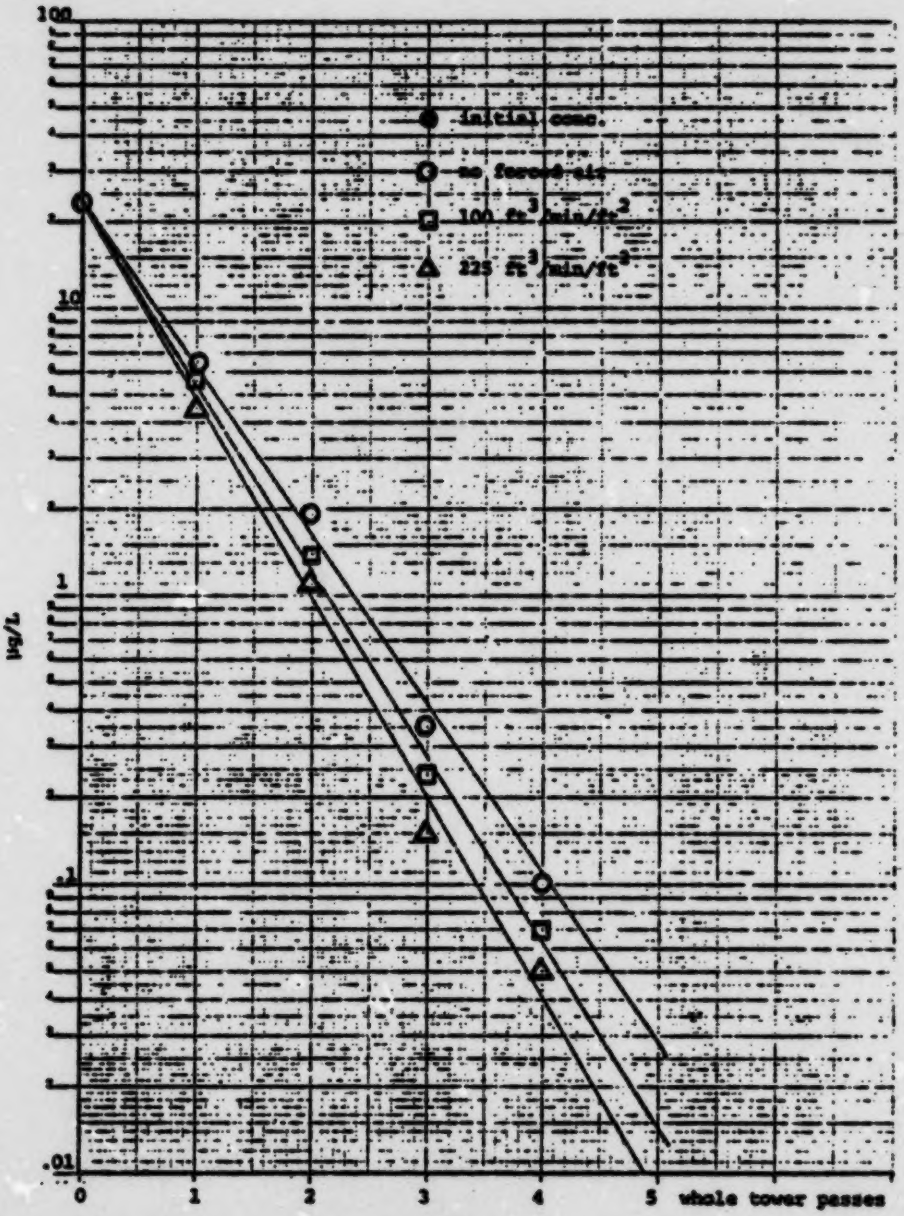


Figure 66 Cis 1,2-dichloroethene rate-loss data in aeration tower, varying air flow (Tests 7, 8 and 9).

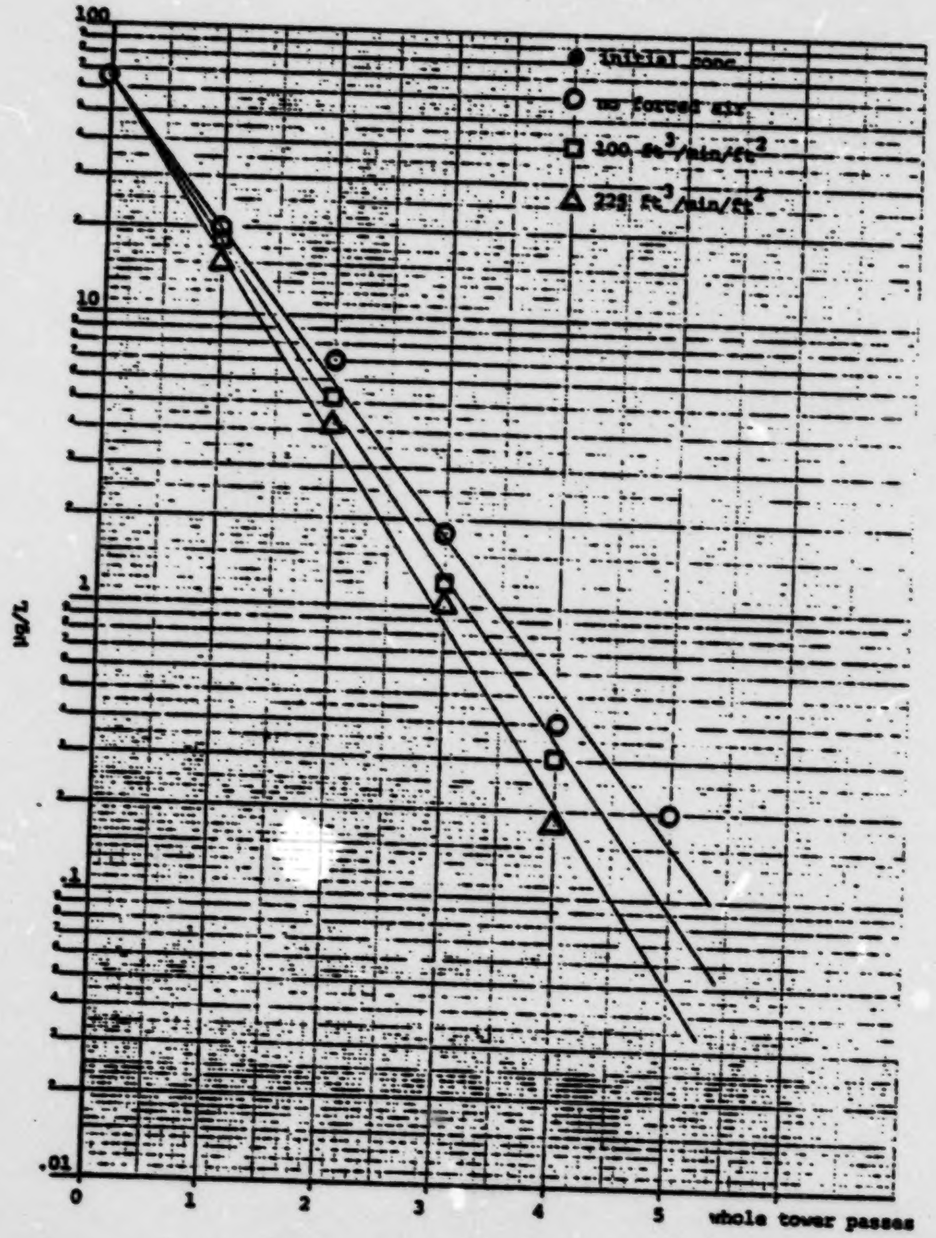


Figure 67 Chloroform rate-loss data in aeration tower, varying air flow (Tests 7, 8 and 9).

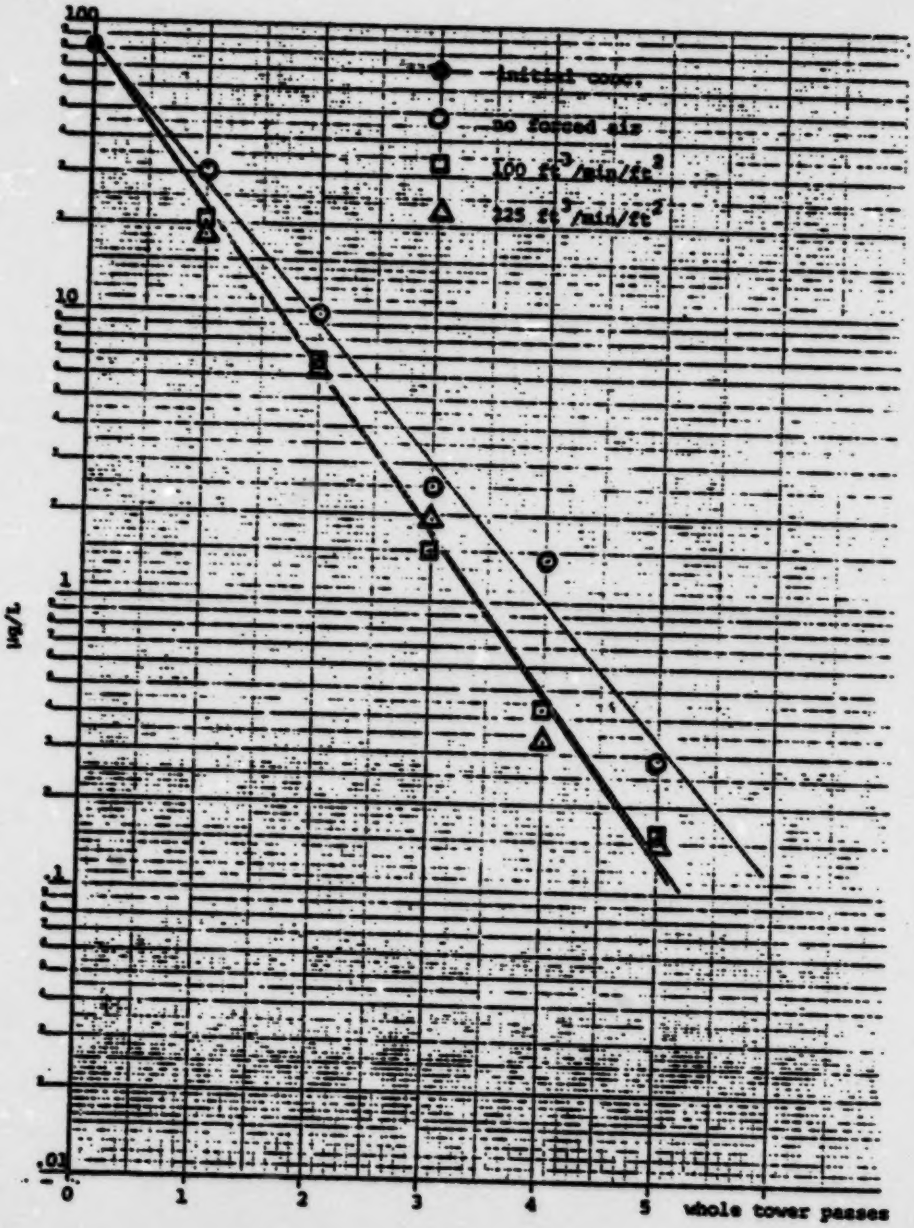


Figure 68 Bromodichloromethane rate-loss data in aeration tower, varying air flow (Tests 7, 8 and 9).

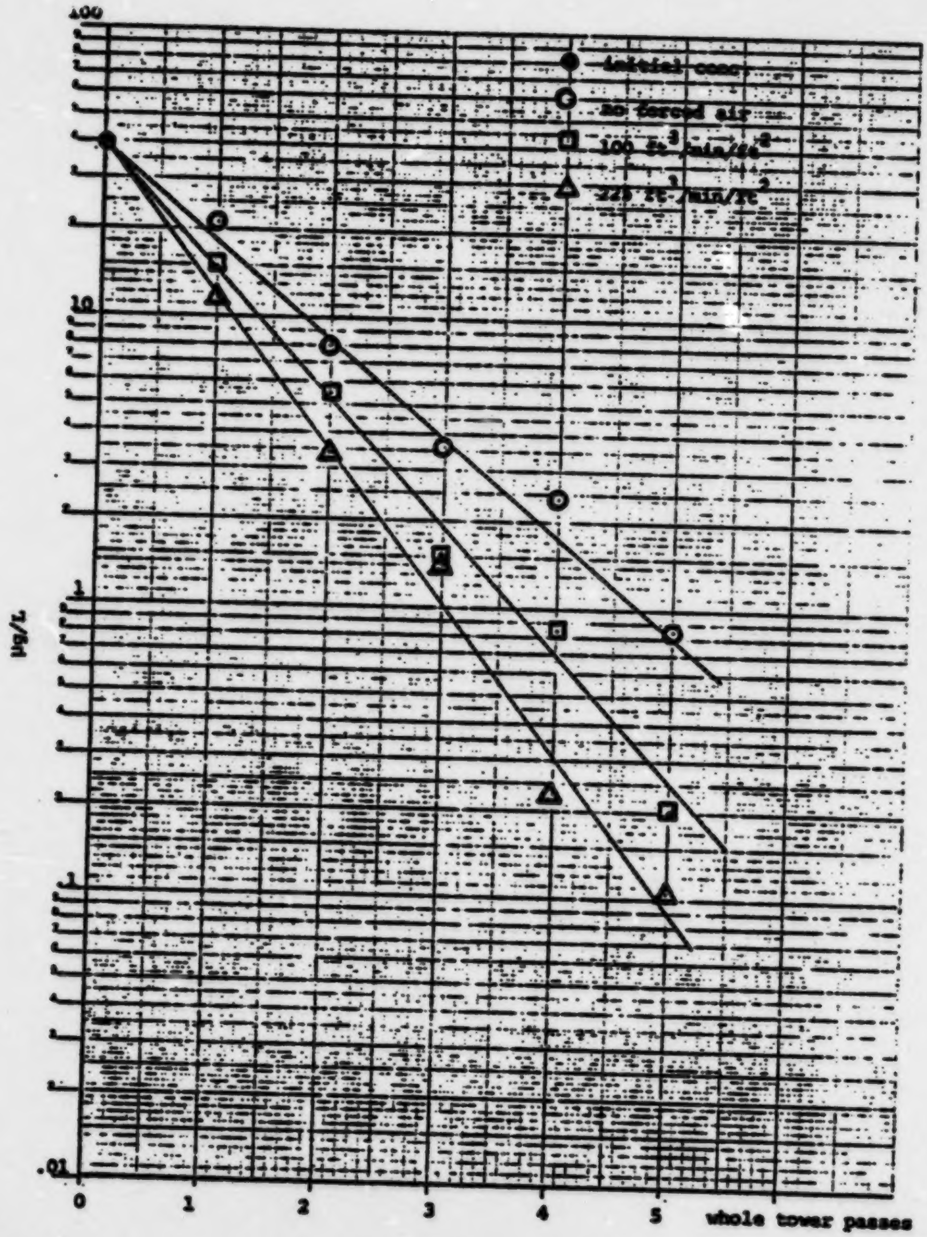


Figure 69 Chlorodibromomethane rate-loss data in aeration tower, varying air flow (Tests 7, 8 and).

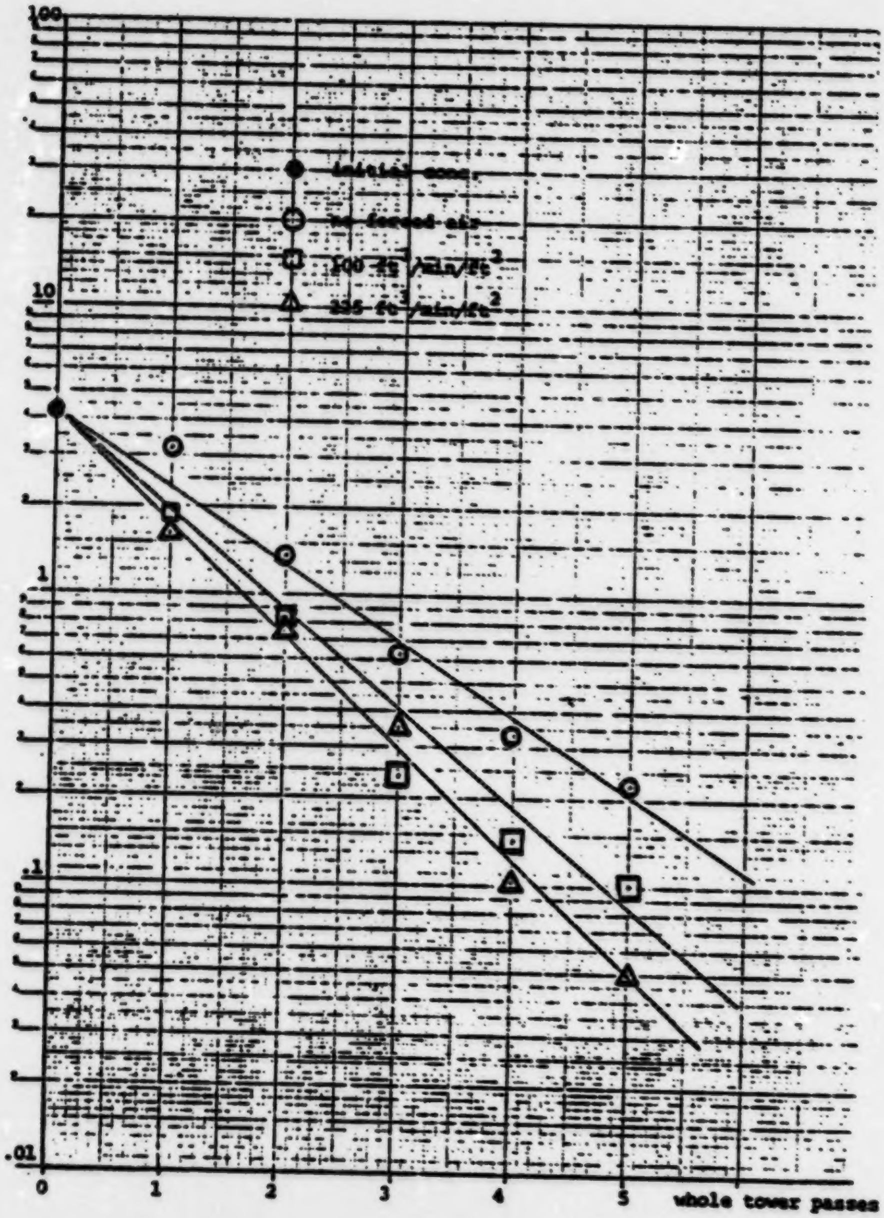


**Figure 70** Bromoform rate-loss data in aeration tower, varying air flow (Tests 7, 8 and 9).

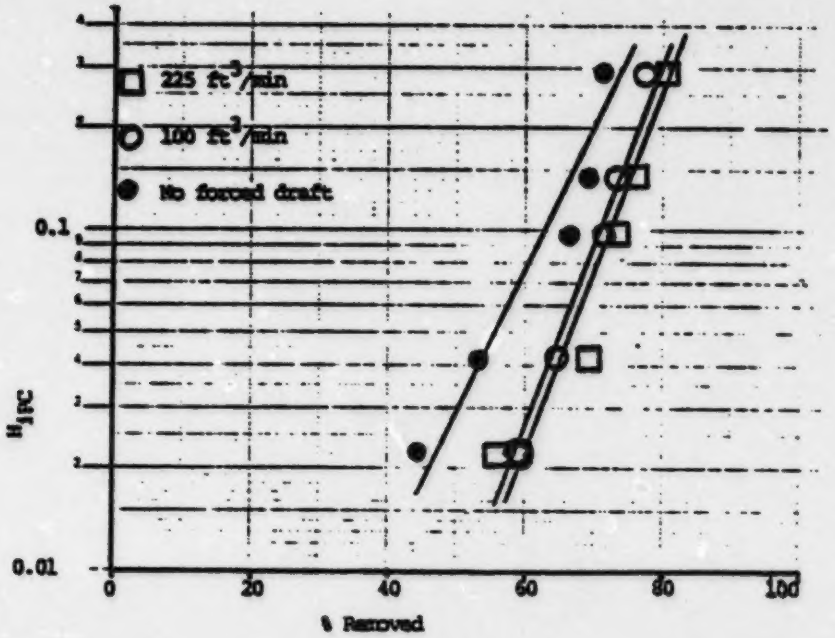


Figure 71 Rate-loss data varying the air flow rate in the aeration tower (Tests 7, 8 and 9).

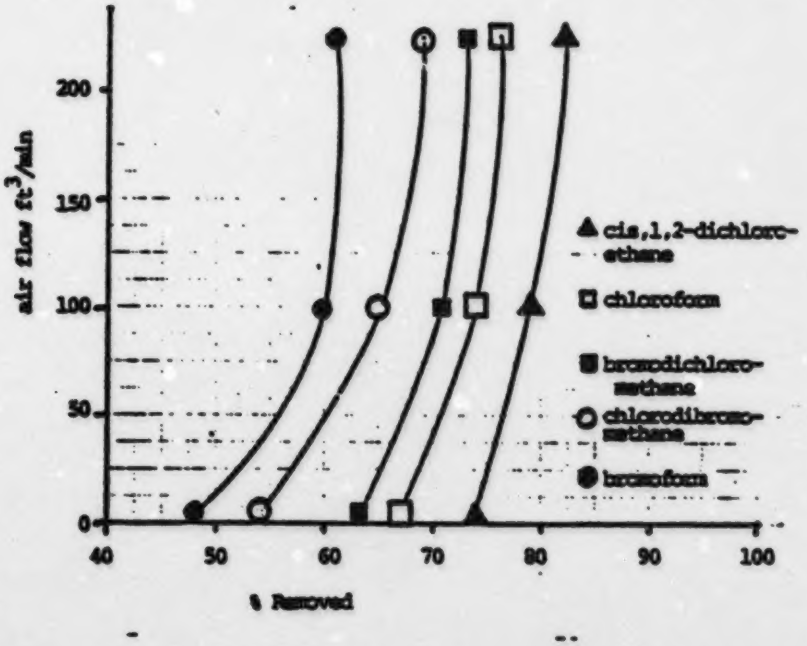


Figure 72 Rectangular plot of data in Figure 71

comparison, the lowest value, 65 percent reduction will be used.

In Figure 66 decreasing the water flow rate from 30 to 15 gal/min/ft$^2$ resulted in the percent loss of chloroform from 78 to 89. Even if the no forced draft value of 65 percent chloroform value is used, the 89 percent removal rate could have been achieved by maintaining the full 30/gal/min/ft$^2$ water flow rate by merely doubling the tower length (65 percent reduction per whole tower pass, 88 percent reduction for two whole tower passes).

In Figure 72, increasing the forced draft from no forced draft to 100 ft$^3$/min, changed the chloroform removal rate from 67 to 74 percent. This could have been achieved by merely increasing the tower length by approximately a half tower length.

Increasing tower length might be the overall less expensive method of achieving a desired percent removal over a long term service use.

### B410 Rate-Loss Through Spray Heads Without Tower

It has been shown that the slope of the rate-loss linear plot, or the percent removal, for the spray head section of the tower indicates greater removal (on a per foot or equal time basis) than by the whole tower or splash bar section of the tower. Therefore, Test 10 was designed to study the effect of spraying water thorugh the spray head section without a tower. The unit shown in Figure 73 was constructed. The same nine-unit spray head from the aeration tower (Figure 50) and the same holding tanks was used. The spray heads were set at a height of nine feet from the mid-point of the holding tanks. Thus, the average free fall of water was nine ft., which was close to the 9.5 ft. for the whole tower height in Figure 50. Tank 1 was filled with finished water and sodium thiosulfate was added as usual to eliminate the free chlorine. With the spray heads over holding Tank 2, the water was pumped at 30 gal/min/ft$^2$ into holding Tank 2. The plastic drop cloth prevented the over-spray water from getting back into holding Tank 1. When Tank 2 received all the water, the water was thoroughly mixed and sampled. The process was then reversed with the spray heads over Tank 1. This was repeated five times. The wind velocity during this study was about average. The rate-loss data from Test 10 are given in Table 45 and plotted in Figure 74. The data points are scattered from this one test run. However, a straight line representing the average values was drawn as shown in Figure 74. The rate-loss line for the whole aeration tower (Figure 49) is also shown for comparison. The two lines are quite close in performance, suggesting that the splash bar section of the tower may not be necessary at all.

### B411 Chloroform Growth Due to Reaction of Free Chlorine with Fiberglass Resin in Holding Tank

As discussed earlier in the report, we had a problem of chloroform growth in the fiberglassed holding tank. Typical data obtained are given in Table 46 and they are plotted in Figure 75. Initial concentration, followed by spray

# TABLE 45

## RATE-LOSS DATA FROM SPRAY HEAD--FREE FALL AERATION STUDY (TEST 10)

μg/L

| | | vinyl chloride | methylene chloride | trans 1,2-dichloroethene | 1,1-dichloroethane | cis 1,2-dichloroethene | chloroform | 1,2-dichloroethane | 1,1,1-trichloroethane | carbon tetrachloride | trichloroethylene | bromodichloromethane | tetrachloroethylene | chlorodibromomethane | chlorobenzene | bromoform | p-chlorotoluene | p-dichlorobenzene | o-dichlorobenzene | benzene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Initial Conc. | | 4.8 | 0.4 | 0.43 | 0.31 | 22.4 | 69.5 | | | .. | 0.18 | 85.4 | 0.14 | 39.1 | 0.35 | 5.7 | | 0.21 | 0.18 | |
| Pass 1 | | nil | 0.24<br>nil | nil | nil | 6.2<br>4.5 | 28<br>24.0 | | | | nil | 46.3<br>39.7 | nil | 19.3<br>17.7 | nil | 4.1<br>2.9 | | nil | nil | |
| % removed | ave. | (100)<br>nil | 0.12 | nil | nil | (76)<br>5.4 | (62)<br>26.0 | | | | nil | (50)<br>43 | nil | (53)<br>18.5 | nil | (39)<br>3.5 | | nil | nil | |
| Pass 2 | | | | | | 1.7<br>0.5 | 9.1<br>5.3 | | | | | 15.1<br>12.3 | | 12<br>8.6 | | 2.5<br>1.7 | | | | |
| % removed | ave. | nil | nil | nil | nil | (80)<br>1.1 | (73)<br>7.2 | | | | nil | (68)<br>13.7 | nil | (44)<br>10.3 | nil | (40)<br>2.1 | | nil | nil | |
| Pass 3 | | | | | | 1.1<br>0.82 | 1.9<br>1.3 | | | | | 6.2<br>3.8 | | 7.5<br>6.1 | | 1.2<br>- | | | | |
| % removed | ave. | nil | nil | nil | nil | 0.96 | (78)<br>1.6 | | | | nil | (63)<br>5 | nil | (34)<br>6.8 | nil | (43)<br>1.2 | | nil | nil | |
| Pass 4 | | | | | | 0.38<br>nil | 1.1<br>0.50 | | | | | 3.7<br>2.5 | | 6<br>2.2 | | 0.8<br>0.42 | | | | |
| % removed | ave. | nil | nil | nil | nil | (80)<br>0.19 | 0.84 | | | | nil | (38)<br>3.1 | nil | (40)<br>4.1 | nil | (49)<br>0.61 | | nil | nil | |
| Pass 5 | | | | | | | 0.16<br>- | | | | | 0.92<br>0.63 | | 1.9<br>1.3 | | 0.63<br>0.33 | | | | |
| % removed | ave. | nil | nil | nil | nil | nil | 0.16 | | | .. | nil | (79)<br>0.64 | nil | (61)<br>1.6 | nil | 0.40 | | nil | nil | |
| average % removed | | | | | | 79 | 71 | | | | | 55 | | 43 | | 43 | | | | |

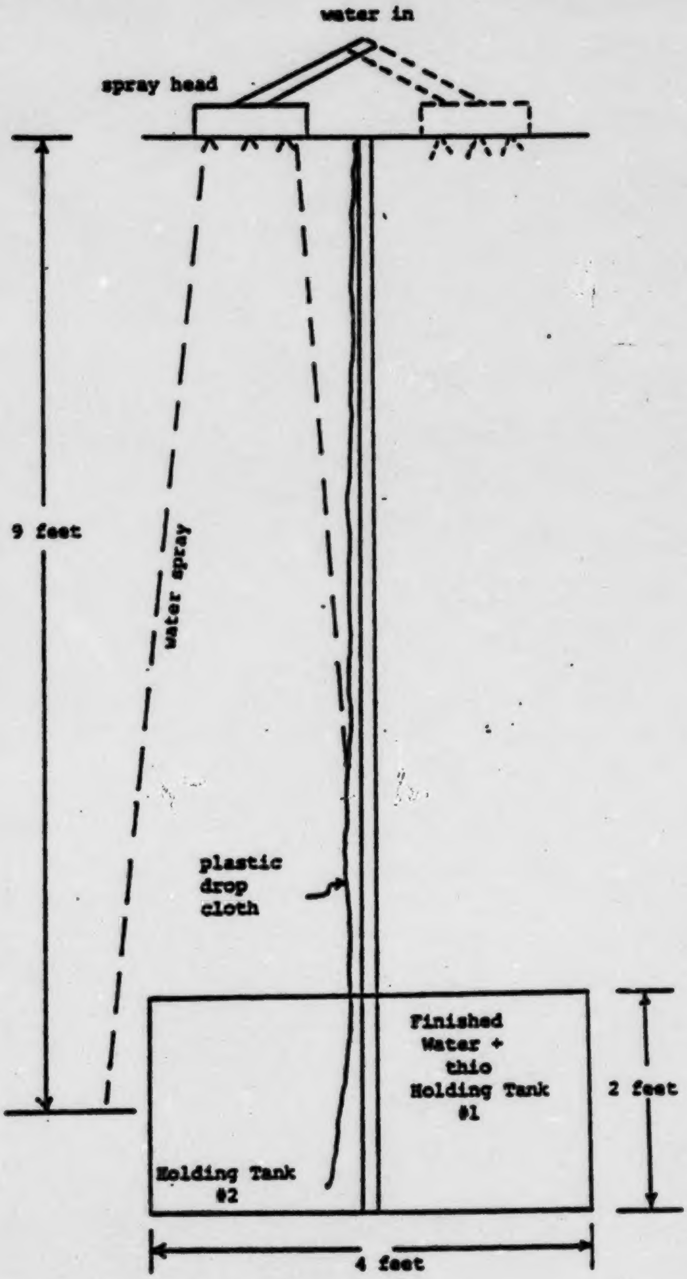

water in
spray head
9 feet
water spray
plastic drop cloth
Finished Water + thio Holding Tank #1
Holding Tank #2
2 feet
4 feet

Figure 73 Apparatus for spray-head free-fall aeration study.

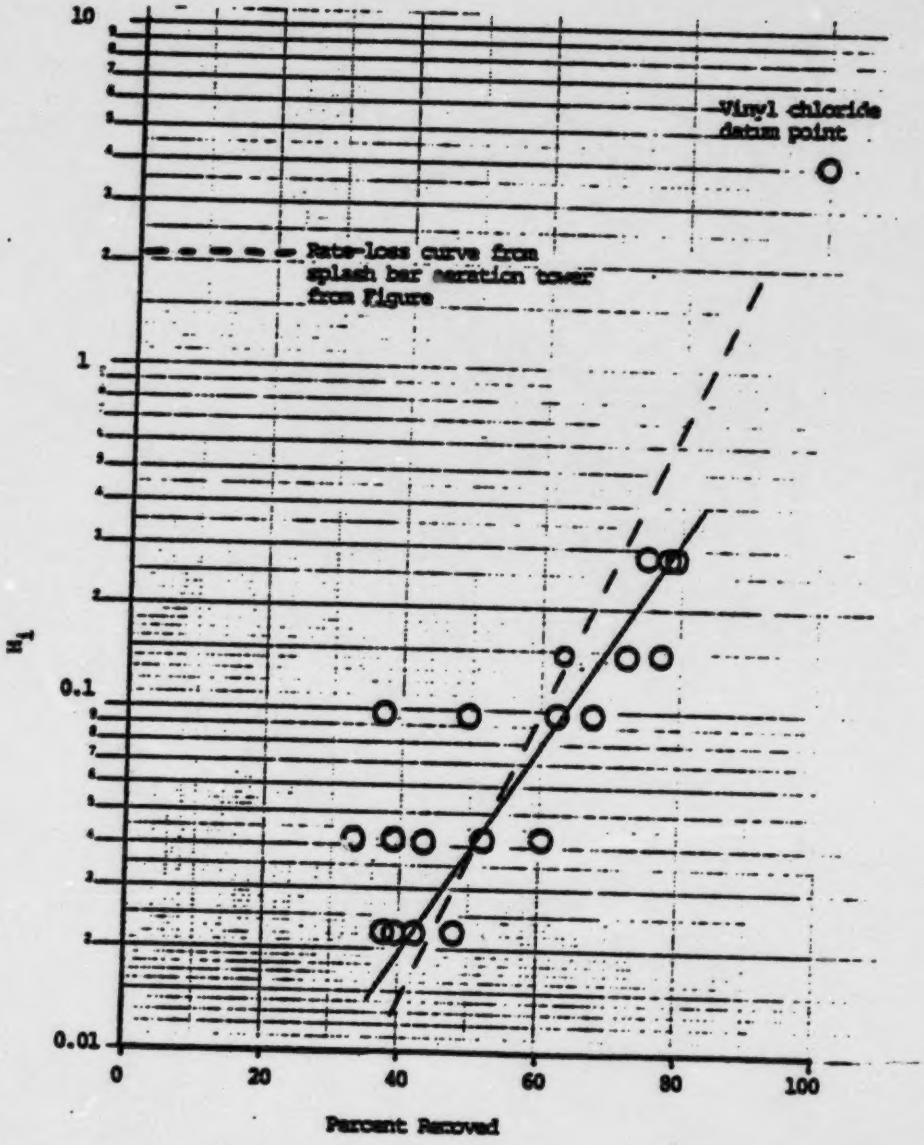


Figure 74 Rate-loss data from spray head study (Test 10)

## TABLE 46

## CHLOROFORM GROWTH IN HOLDING TANK

| Sample Point | Chloroform concentration in µg/L |
|---|---|
| Fin. Water T. | 89 |
| $SH_1$ | 70 |
| $8_1$ | 45 |
| $T_2$ | 64 |
| $SH_2$ | 56.5 |
| $8_2$ | 39.5 |
| $T_3$ | 51.8 |
| $SH_3$ | 46 |
| $8_3$ | 40 |
| $T_4$ | 47.5 |
| $SH_4$ | 42 |
| $8_4$ | 38.5 |
| $T_5$ | 43 |
| $SH_5$ | 39.3 |
| $8_5$ | 35 |

$T_1$ = tank No. 1

$SH_1$ = first spray head pass

$8_1$ = first 8 foot splash bar section pass

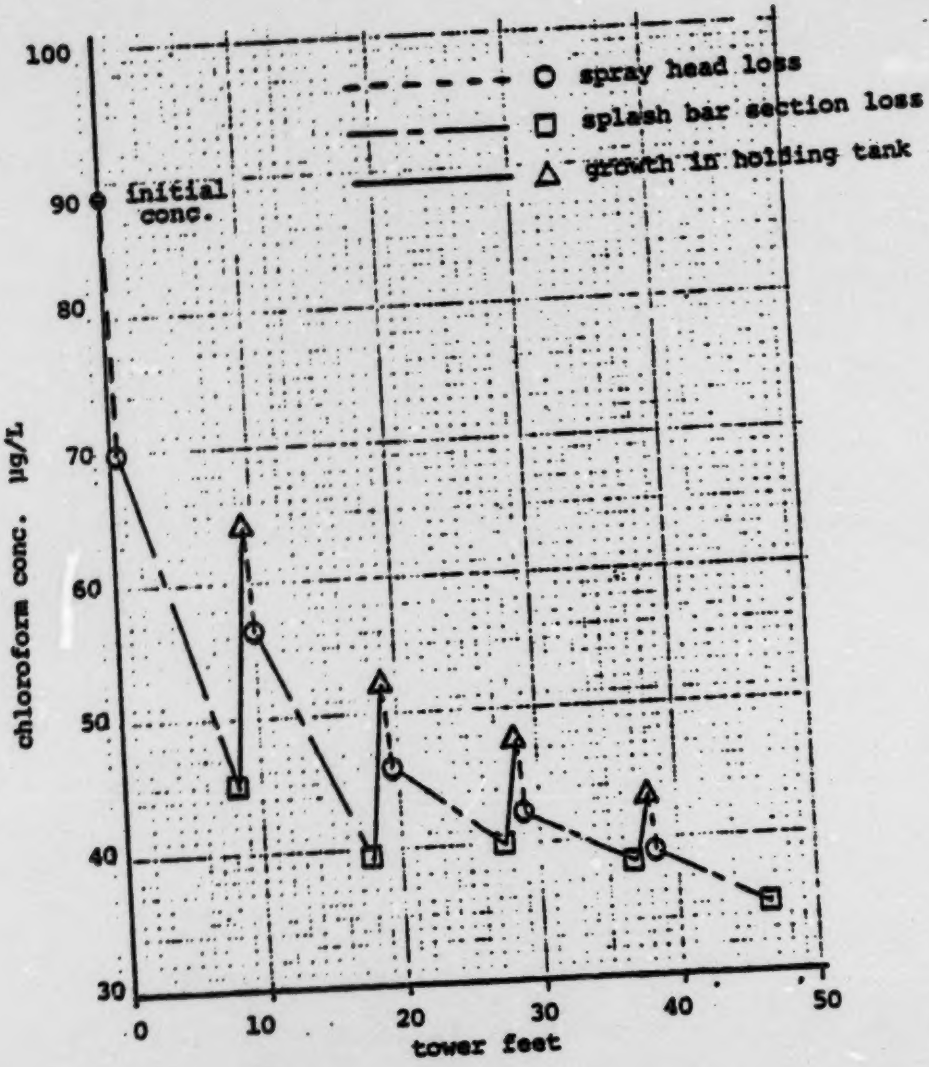


Figure 75 Chloroform growth in holding tank

head loss, followed by loss in eight ft. splash bar tower section, followed by chloroform growth in the holding tank is apparent. The retention time in the holding tank was approximately 6.5 minutes for Tank 1, decreasing for the following tanks as water was lost due to spillage. Chloroforom growth in the holding tank decreased with each pass mainly because the level of free chlorine decreases with each pass due to aeration loss.

### B412 Rate of Free Chlorine Loss and Oxygen Uptake

Initial concentration and loss after repeated tower passes of free and combined chlorine and dissolved oxygen in finished water are shown in Table 47. The initial concentration of dissolved oxygen was 5.4 ppm and after one tower pass it reached its maximum concentration, leveling off at approximately 8 ppm. The lower dissolved oxygen values for the fourth and fifth tower passes may only be analytical error. The combined chlorine level appeared to be unaffected by passing through the tower.

This work was done using glass tanks to avoid free chlorine loss due to reacting with the fiberglass resin. The initial concentration of free chlorine was 2.3 ppm and the level dropped with each tower pass. The data are plotted in Figure 76, log concentration against tower passes. The rate-loss of free chlorine was quite close to the rate-loss for bromform. As expected, there was no detectable loss of TOC even after five tower passes.

### B413 Conclusions from Aeration-Tower Study

1) In an aeration tower (or some other aeration system where the concentration in the water phase, although continually decreasing, is uniform throughout the water column) the rate-loss of organic contaminants is linear when plotted with log concentration versus time (or tower length).

2) The algebraic slope of the line equals:

$$\frac{\ln \frac{C_i}{C_{io}}}{t - t}$$

where $C_{io}$ = initial concentration of compound i in the water at time $t_1$ the
$C_i$ = concentration of compound i in the water at time $t_2$
$t_1$ = initial starting time
$t_2$ = the time at which $C_i$ is measured

3) When t is chosen such that $C_i$ is one-half of $C_{io}$, t is half life $t_{1/2L}$. At $t_{1/2L}$, the slope becomes:

$$\frac{0.6931}{t_{1/2L}}$$

### TABLE 47

### EFFECT OF AERATION TOWER ON DISSOLVED OXYGEN, FREE AND COMBINED CHLORINE, TOC AND THMFP

No Forced Draft - 30 gal/min/ft$^2$

| | Dissolved oxygen ppm | Free chlorine ppm | Combined chlorine ppm | TOC ppm |
|---|---|---|---|---|
| Finished Water | 5.4 | 2.3 | 0.55 | 5.4 |
| 1 aeration tower pass | 8.0 | 2.07 | 0.43 | 5.2 |
| 2 " | 8.0 | 1.45 | 0.44 | 5.2 |
| 3 " | 7.9 | 1.4 | 0.45 | 5.4 |
| 4 " | 7.6 | 1.28 | 0.66 | 5.2 |
| 5 " | 7.6 | 0.9 | 0.35 | 5.3 |

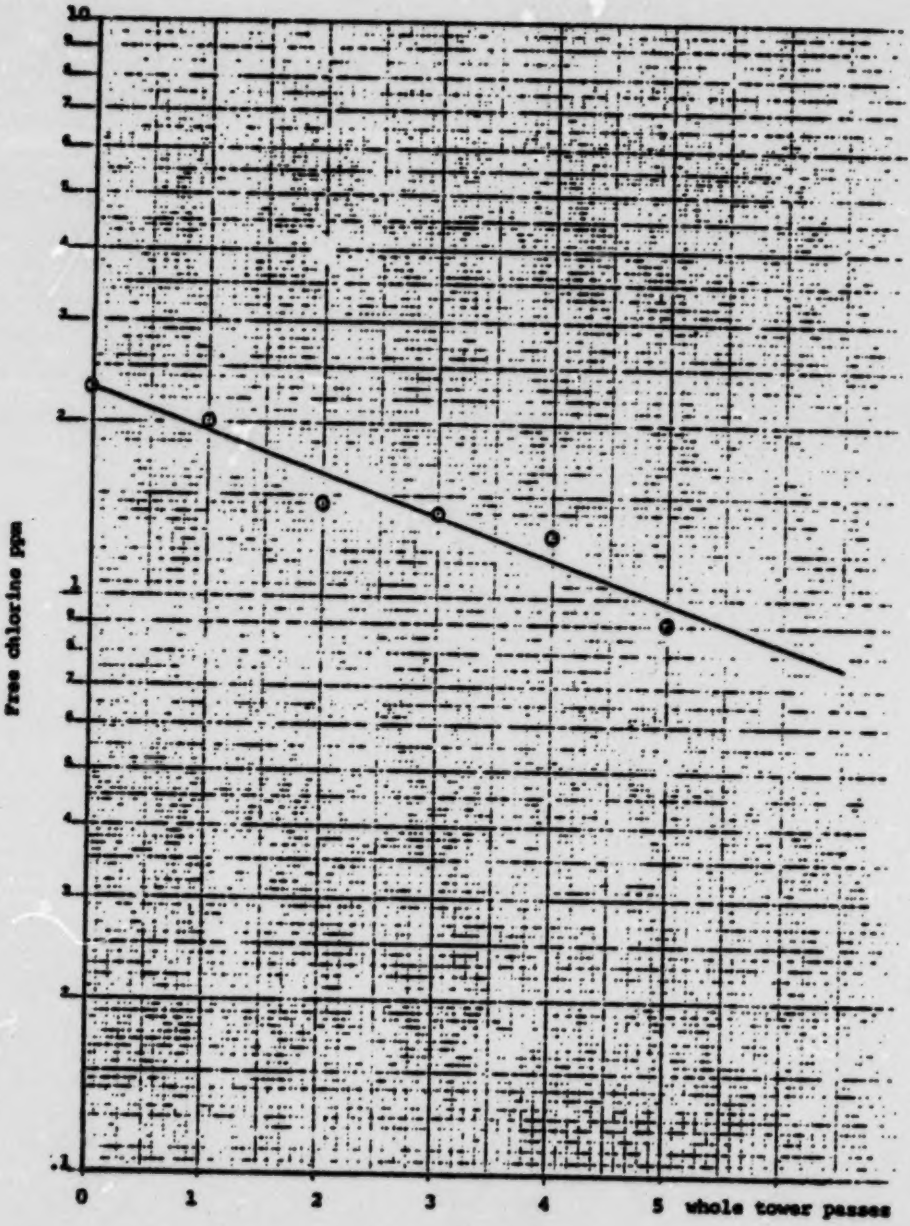


Figure 76 Rate-loss of free chlorine in aeration tower.

3) The rate-loss of an organic contaminant from water (the slope of the linear plot), is independent of other organic compounds when all compounds present are completely soluble.

4) The rate-loss is independent of concentration in the range of solubility. Compounds were tested as high as 2200 μg/L with total mixed concentrations up to 500 μg/L.

5) A plot of the log of the partition coefficient ($H_{iPC}$) versus slope is linear for a broad family of compounds.

6) This linear plot (log $H_{iPC}$ versus slope) can be established experimentally for a given aeration system with two compounds. If the $H_{iPC}$ for any other compound in the broad family is known, its rate-loss can be predicted.

7) The family of compounds probably includes most volatile organic contaminants of concern in drinking water, which are not reactive with the water and have an $H_{iPC}$ value above 0.02. Below this value, rate-loss is still probably linear in such a plot for other families of compounds. The slope of the linear plot will be different for each family.

8) By measuring the rate-loss in the spray head section and the splash bar section of a pilot tower, one can predict the length of splash bar section required for a plant tower to achieve any desired removal.

9) In a given tower, lowering the water flow rate increases the rate-loss.

10) As the severity of aeration parameters increase; e.g., interfacial area and air velocity over the interface increases, the change in rate-loss of compounds is not constant. The increase is greater the greater the $H_{iPC}$ value.

11) In a given aeration system, increasing the air flow increases the rate-loss.

12) In a baffled aeration tower as designed in this study, merely increasing the tower length may be less expensive over a long operation period compared to achieving a given rate-loss by reducing the water flow rate or increased air flow rate.

13) Using the same spray head employed in our aeration tower work we achieved almost the same rate-loss in a nine foot free-fall with no tower, as achieved with nine ft. of splash bar tower section (no forced draft).

14) The $H_{iPC}$ value for vinyl chloride is probably in the 4.2 to 5.2 range.

15) Chloroform was rapidly produced when water containing free chlorine was stored in fiberglassed resin coated holding tanks. We presume the chloroform resulted from the reaction of free chlorine with the resin. We show the

amount produced, but did not evaluate production over a long time period to determine whether or not it ever decreased. Several months of intermittent use did not seem to alter the production rate. We avoided the problem by combining the free chlorine with sodium thiosulfate.

16) The rate-loss of free chlorine in an aeration tower was studied. A plot of log concentration versus time (or tower length) appears to be linear. In our system, the rate-loss of free chlorine was close to the rate-loss of bromoform.

17) The combined chlorine appeared to be unaffected by even five tower passes.

18) The initial concentration of dissolved oxygen in our finished water was 5.4 ppm. One pass through the tower increased the level to 8 ppm. This value is probably the maximum attainable since further tower passes showed no increase.

19) As expected, even five passes through the tower had no appreciable effect on TOC levels.

# APPENDIX C

## EXPERIMENTAL DESIGN 3:
## DETERMINING THE SOURCE OF VOLATILE CHLORINATED ORGANICS IN RAW INFLUENT TO THE PRESTON PLANT

### C1 Chemical and Biological Parameters

### C11 Introduction

Chloroform and other THM, which present a potential health hazard to man, are generated in the water treatment plant by the reaction of chlorine on naturally occurring organic substances in the raw water. These organic substances are probably not harmful in their natural state. Modification of water treatment plant and distribution system practices are obviously our major research concern to eliminate or minimize the level of THM in drinking water. However, another problem has been identified in Miami that must also be solved. Raw water feed to our water treatment plants, drawn from wells approximately 90 ft. deep located on the plant sites, already contains other chlorinated organic compounds, which should be removed. The bulk of these organics consist of a chemical family group, the chlorinated ethenes. These are, vinyl chloride, vinylidene chloride, trans 1,2-dichloroethene, cis 1,2-dichloroethene, trichloroethylene, and tetrachloroethylene. These compounds total approximately 40 to 50 μg/L in the raw water entering the Preston Water Treatment Plant. This chemical family of compounds is potentially more toxic to humans than the THM. ED 3, was designed to determine the source of these compounds in the raw water.

### C12 Identification and Magnitude of the Chloroethene Problem

### C121 Miami, Florida

In previous research work, Ref. 1 thru 6, and this project, continuous background information on 19 specific halogenated organics in raw, lime softened, and finished water at the Preston Water Treatment Plant has been compiled. Average levels for these compounds are given in Table 48. At the Preston plant, the level of trihalomethanes in raw water was nil, and in finished water they accounted for approximately 87 percent of the total halogenated organics (215 of the 245 μg/L). Reasons for the decline or increase from raw to finished water for all the compounds in Table 46 as well as various methods of removal are discussed in Ref. 2 and 3.

Also presented in Table 48 are background data on halogenated organics for a four month period at the Hialeah treatment plant, which is adjacent to the Preston plant. Obviously, the presence of non-trihalomethane halogenated organics is not limited to the Preston water. The level of chloroethenes in

## TABLE 48

## VOLATILE HALOGENATED ORGANICS IN RAW, LIME-SOFTENED AND FINISHED WATER AT THE HIALEAH AND PRESTON TREATMENT PLANTS

| | Average Concentration (μg/L) | | | | | |
|---|---|---|---|---|---|---|
| | Preston Plant | | | Hialeah Plant | | |
| CHEMICAL NAME | Raw Water | Lime Soft. Water | Fin. Water | Raw Water (H-1) | Lime Soft. Water (H-3) | Fin. Water (H-5) |
| **Vinyl Chloride | 12.0 | 8.0 | 7.0 | 5.5 | 5.7 | 3.8 |
| Methylene Chloride and/or Vinylidene chloride | 0.5 | 0.3 | 0.5 | 0.8 | 0.4 | 0.7 |
| **trans 1,2-Dichloroethene | 1.0 | 0.8 | 0.6 | 0.4 | 0.3 | 0.3 |
| 1,1-Dichloroethane | 0.6 | 0.5 | 0.4 | 3.4 | 2.8 | 3.0 |
| **cis 1,2-Dichloroethene | 26.0 | 21.0 | 18.0 | 6.9 | 5.3 | 3.5 |
| *Chloroform | N | 2.0 | 85.0 | 0.2 | 3.3 | 96.0 |
| 1,1,1-Trichloroethane | 0.05 | 0.04 | 0.03 | 0.02 | 0.01 | N |
| 1,2-Dichloroethane | 0.1 | 0.05 | 0.03 | 0.02 | 0.03 | 0.05 |
| Carbon Tetrachloride | 0.05 | 0.05 | 0.05 | N | N | 0.02 |
| **Trichloroethylene | N | 0.3 | 80.0 | 0.5 | 0.5 | 0.4 |
| *Bromodichloromethane | N | 0.8 | 40.0 | 0.07 | 2.2 | 53.0 |
| **Tetrachloroethylene | trace | trace | trace | N | 0.01 | 0.01 |
| *Chlorodibromomethane | N | N | 10.0 | 0.06 | 1.3 | 37.0 |
| Chlorobenzene | 0.7 | 0.6 | 0.6 | 7.5 | 6.3 | 7.0 |
| *Bromoform | N | N | N | 0.10 | 0.12 | 5.3 |
| p-Chlorotoluene | N | N | N | 1.0 | 0.9 | 0.8 |
| m-Dichlorobenzene | N | N | N | N | N | N |
| p-Dichlorobenzene | 0.3 | 0.3 | 0.2 | 0.6 | 0.5 | 0.5 |
| o-Dichlorobenzene | 0.2 | 0.2 | 0.2 | 1.7 | 1.5 | 1.2 |

N = Nil
Preston Plant - Jan. 1976 - Jan. 1978
Hialeah Plant - Mar. 1979 - July 1979
*trihalomethanes - Preston Total in Fin. Water 215 μg/L
Hialeah Total in Fin. Water 191 μg/L
**chloroethenes - Preston Total in Raw Water 40 μg/L
Hialeah Total in Raw Water 13 μg/L

raw water was 40 and 13 µg/L, respectively, for the Preston and Hialeah plants.

### C122 State of Florida

In 1978, a joint study "Survey of Trihalomethane Distribution in Various Potable Water Supply Sources in the State of Florida (Ref. 26) was carried out by the Department of Environmental Regulation, Tallahassee, Florida and the Drinking Water Research Center of Florida International University. In this survey, 116 water facilities were studied. Although the analytical procedures were designed to optimize the determination of THM an idea of the prevalence of chloroethenes can be obtained from Table 49.

Twenty of the 116 facilities showed significant levels of chloroethenes. These facilities are listed in order of their maximum concentration levels. The level of total chloroethenes ranged from 1.4 to 225.7 µg/L in raw water. In 1978 Vero Beach water had the highest level. In 1980, the concentration level at Vero Beach was much lower. Later in this report, Vero Beach water will be disucssed in more detail.

## C13 Some Preliminary Considerations of Source

### C131 Recharge of Wells by Finished Water

The seven wells that supply the Preston Plant are located on the plant site (one is nearby) and the immediate adjacent area is mostly residential. It was conceivable that finished water; e.g., lawn sprinkling, could percolate down and re-enter the wells. Immediately, questions were raised regarding this possible source. The raw water contained almost nil levels of THM, which predominates in the finished water. The concentration of chloroethenes in raw water was always above the levels in finished water. Thus, recharge of wells by finished water did not seem likely.

### C132 Recharge of Wells by Chlorinated Sewage Effluent

No sewage effluent, chlorinated or otherwise, drained near the plant site. However, this possible source was still considered. The halogenated organic profile from a local sewage plant, before and after chlorination, is shown in Table 50. Here again, THM's predominate (184 µg/L) and yet they are not found in the well water. Considerable vinyl chloride (16 µg/L) was generated, but there was no vinylidene chloride, or trans and cis 1,2-dichloroethene present, and only a trace of tetrachloroethylene. Repeated surveys of canals near the water treatment plants showed no traces of chloroethenes or THM. Chlorinated sewage effluent did not seem to be a likely source.

# TABLE 49

## PREVALENCE OF CHLOROETHENES IN RAW WATER IN FLORIDA (1978)

| | conc. μg/L | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| PUBLIC UTILITY | water source | vinyl chloride | vinylidene chloride | trans 1,2-dichloroethene | cis 1,2-dichloroethene | trichloro-ethylene | tetrachloro-ethylene | TOTAL |
| City of Vero Beach | wells | 12 | 1.5 | - | 124 | 87 | 1.2 | 225.7 |
| City of Vero Beach (Apr. 1980) | " | nil | 0.17 | 0.08 | 2.4 | 0.84 | nil | 3.5 |
| North Miami Beach | " | 64 | 1.4 | - | 10 | 1 | - | 76.4 |
| Miami-Dade Water & Sewer Authority, (Preston Plant) | " | 13 | 0.5 | 1.5 | 26 | 0.5 | 0.03 | 41.5 |
| Miami-Dade Water & Sewer Authority, (Hialeah Plant) | " | 6.2 | 0.5 | 1.5 | 6.9 | 0.5 | 1.1 | 16.7 |
| Pompano Beach | " | - | - | - | - | 19 | - | 19 |
| Riviera Beach | " | 11 | - | - | 3 | - | - | 14 |
| Broward County Utility | " | - | - | - | 7 | 1.6 | 1.9 | 10.5 |
| Pensacola Pub. Utility | " | - | - | - | 6 | 2.7 | - | 8.7 |
| City of Hallandale | " | - | - | - | 1.4 | 7.2 | - | 8.6 |
| City of Mariana | " | 6.2 | - | - | - | - | 1.1 | 7.3 |
| City of Hollywood | " | 3.8 | - | - | - | - | - | 3.8 |
| Panama City | lake | 3.7 | - | - | - | - | - | 3.7 |
| North Palm Beach | wells | - | - | - | - | 1.2 | 2.2 | 3.4 |
| Ft. Pierce | " | - | - | - | - | - | 3.3 | 3.3 |
| City of Bartow | " | 3.3 | - | - | - | - | - | 3.3 |
| Ft. Myers | " | - | - | - | - | 3.1 | - | 3.1 |
| Stuart | " | - | - | - | 3 | - | - | 3 |
| Englewood | " | 1.7 | - | - | - | - | - | 1.7 |
| Plantation | " | 1.7 | - | - | - | - | - | 1.7 |
| Lakeland | " | 1.4 | - | - | - | - | - | 1.4 |

## TABLE 50

## HALOGENATED ORGANIC PROFILE OF CLARIFIED SEWAGE EFFLUENT BEFORE AND AFTER CHLORINATION (MIAMI AREA)

| | µg/L Sewage Treatment Plant Clarified Effluent | |
|---|---|---|
| | Before Chlorination | After Chlorination |
| Vinyl Chloride | ND | 16 |
| Methylene Chloride | .12 | .07 |
| Vinylidene Chloride | ND | ND |
| Trans 1,2-Dichloroethene | ND | ND |
| 1,1-Dichloroethane | ND | ND |
| Cis 1,2-Dichloroethene | ND | ND |
| Chloroform | 1.9 | 157* |
| Trichloroethylene | ND | ND |
| Bromodichloromethane | .4 | 25* |
| Tetrachloroethylene | .06 | .04 |
| Chlorodibromomethane | .2 | 1.7* |
| Chlorobenzene | ND | ND |
| Bromoform | ND | ND |
| p-Chlorotoluene | ND | ND |
| m-Dichlorobenzene | ND | ND |
| p-Dichlorobenzene | .6 | 1.1 |
| o-Dichlorobenzene | ND | ND |

*THM's

ND= none detected

Assessing the makeup of the chloroethene compounds in raw water revealed that all of them could be accounted for by some type of breakdown or degradation of the higher molecular weight chloroethenes, e.g. tri- and tetrachloroethylene. All the possible chlorinated degradation products of tetrachloroethylene containing only carbon, hydrogen and chlorine, breaking the double bond but not saturating it, are shown in Table 51. All the compounds in Table 51 were routinely found in raw water, although the concentration of methyl chloride was always very low.

Tetrachloroethylene and trichloroethylene and other volatile chlorinated organics are used in enormous quantities nationwide in urban communities for fiber, fabric and metal degreasing. The 1979 U.S. production of four such compounds is shown in Table 52.

TABLE 52

ANNUAL U.S. PRODUCTION (1979) OF
FOUR CHORINATED SOLVENTS

| | lbs. |
|---|---|
| Methylene Chloride | 625,000,000 |
| 1,1,1-Trichloroethane | 700,000,000 |
| Trichloroethylene | 325,000,000 |
| Tetrachloroethylene | 750,000,000 |
| Total | 2,400,000,000 |

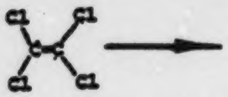
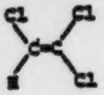
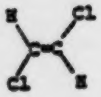
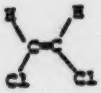
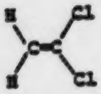
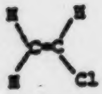
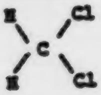
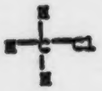
The compounds in Table 52 are used in such a way that virtually all of the production going to degreasing uses essentially passes into the atmosphere. However, a small amount enters the surface and ground waters by accidental spillage.

The possibility of such spillage in surface waters and the breakdown into other chloroethene compounds of lower molecular weight by ultraviolet degradation was considered as a source of raw groundwater contamination.

Trichloroethylene and tetrachloroethylene were individually added to water in a balanced fresh water aquarium in bright sunshine and monitored for halogenated organic composition changes. Only intermittent traces of some of the lower chlorinated degradation products were found. The work was repeated in sealed quartz tubes with the same result. While we recognized that our U.V. work was limited in scope, it appeared to us that U.V. degradation was probably not the source of lower chloroethene species. In addition, repeated monitoring of the network of freshwater canals, which serve as one source of replacement water for the wells at the Preston and Hialeah plants, indicated no trace of any halogenated organic compounds. Dilling, Bredeweg and Tefertiller (Ref. 27) did considerable work on simulated atmospheric photodecomposition of the chlorinated compounds studied in this report. The rates of

TABLE 51

POSSIBLE CHLORINATED DEGRADATION PRODUCTS OF TETRACHLOROETHYLENE (CONTAINING ONLY CARBON, HYDROGEN, CHLORINE, BREAKING DOUBLE BOND BUT NOT SATURATING IT)

| | | | |
|---|---|---|---|
| <br>tetrachloroethylene |  | trichloroethylene | chloroethenes |
| |  | trans 1,2-dichloroethane | |
| |  | cis 1,2-dichloroethane | |
| |  | vinylidene chloride | |
| |  | vinyl chloride | |
| |  | methylene chloride | chloromethanes |
| |  | methyl chloride | |

decomposition varied widely (in the presence of other chemical substances), but no mention was made of lower molecular weight members of the families being formed. At this point, it seemed that perhaps biodegradation of the higher molecular weight chloroethenes accidentally entering the aquifer was a possible explanation of the existence of these compounds in ground water.

## C14 Biodegradation as a Source

### C141 Biodegradation Literature Review

The role that microorganisms in soil and water have on specific toxic organic contaminants, their ability or lack of ability to detoxify or mineralize, is becoming more of a concern to the whole scientific community. This subject has been summarized by Alexander (Ref. 28). If a toxic organic chemical is converted to a non-toxic organic chemical by microbial activity, the biological process results in detoxification. If the end result is carbon dioxide, water and inorganic products the process is called mineralization. If innocuous compounds are converted to toxicants, the process is known as activation. In the latter case, the microorganisms themselves are agents of pollution.

Barth and Bunch (Ref. 29) have added considerable information to the field of biodegradation of specific pollutants. They presented the following 1) Ultimate Degradation — conversion of parent compound to carbon dioxide, water and inorganic compounds. 2) Primary Degradation — A change in the parent compound such that it no longer responds to the analytical measurement used for detection. 3) Acceptable Degradation — Conversion of the parent compound to the extent that undesirable properties are no longer manifest.

The National Academy of Sciences (Ref. 30) has reviewed the literature on the possible mechanism for degradation or transformation of low molecular weight halogenated compounds in natural water systems, including chemical, photochemical and biologically mediated reactions. They speak of a "dearth of specific information" in this area. They cite emissions from anthropogenic production and use as the major source of carbon tetrachloride and methylene chloride in the environment. Essentially all of the methylene chloride manufactured enters the atmosphere as a result of dispersive losses from its end use as a solvent and degreaser. The estimated world production of methylene chloride in 1973 was 400 x $10^3$ tons/yr. McConnell (Ref. 31). In the United States, emissions of methylene chloride are estimated at 84 percent of the annual production. Dilling et al. (Ref. 27) and Cox et al. (32) report long atmospheric half lives for methylene chloride, 250 hours and 0.2 years respectively, yet McConnell, Ferguson and Pearson (Ref. 31) did not find it in human tissues, nor in dairy products, livestock meats, edible fats and oils, fruits or vegetables or beverages. We are fortunate that apparently it is not persistent in the environment. If this is true, where does it go? McConnell et al. (Ref. 31) indicated that there is evidence that some of the one- or two- carbon chlorinated methanes can be metabolized by mammalian tissues, but not by microorganisms. Our results indicated a rapid biodegradation rate for methylene chloride. We show that biodegradation is probably dependent on the bacterial population composition. Many other factors of bacterial ecology must be involved and we should expect to find extremes in biodegradation results from one geographic location to another, and in the same location at different periods of the year as environmental changes occur. While preparing this report, Rittmann and McCarty (33) reported evidence of biodegradation of methylene chloride.

## C142 Development of Methodology for Biodegradation Studies

We attempted to simulate the conditions that exist in the aquifer and its recharge basin in sealed septum bottles that provided a closed system and contained the volatile compounds, which we provided as metabolites and expected as products of biodegradation. We assumed that the lower weight chloroethenes were formed from commonly used organic solvents in highly organic sediments, which would tend to be anoxic. We knew that submerged Everglades Muck that underlies the aquifer recharge basin has low (<0.1 mg/L) to undetectible concentrations of oxygen 1 CM beneath its surface. The muck was determined to consist of 98% organic matter (determined by loss on ignition) and the surface water contained from 25 to 45 mg/L total organic carbon (TOC), which rapidly depleted measurable dissolved oxygen as determined with an electrode.

Following is a general description of the methods we used. Ten mL of screened fresh muck was placed in 60 mL septum vials, and surface water from the muck sample site was added to fill the vials. From 5 to 20 microliters of a 20 µg/ L methanol solution of the chlorinated compound was then added and the vials quickly sealed with Teflon septa. The vials were either completely filled with water, allowing no air head space, or a predetermined head space volumes were used. We found it necessary to prepare replicate sealed vials for analyses over an extended period and sampled one vial only of each sample series at each time point outlined in the experimental design. This avoided repeated sampling from a single vial, which causes chemical and bacterial contamination and varying head space.

If initial head space or variable head space occured during a test, a chemical mass balance was still obtained. Partitioning of the chemicals between the water and air phases was determined using the following equation developed in Ref. 34:

$$\frac{C_{ie}}{C_{io}} = \frac{1}{1 + \frac{Hi}{Rt} \cdot \frac{Va}{Vw}} \qquad (10)$$

where:

$C_{ie}$ = concentration of compound initially in the water at equilibrium (grams/liter)
$C_{io}$ = original concentration of compound initially in the water (grams/liter)
$H_i$ = a Henry's Law constant (atm $m^3$/mole)
R = the gas constant ($8.2 \times 10^{-5}$) ($m^3$atm g $mol^{-1}$ $K^{-1}$)
t = absolute temperature (K)
$V_a$ = volume of air ($m^3$)
$V_w$ = volume of water ($m^3$)

The chlorinated solvents selectively adsorbed to muck. After addition and shaking for thirty minutes, approximately 88% of the tetrachloroethene was recovered from vials containing muck and water. This recovery was based on analyzing only the water phase after the muck settled and basing the calculation on the total volume of muck and water. The recovered value was used as the initial concentration. When culture media were used instead of muck loss by adsorption did not occur. Because of adsorption by the muck, a true mass balance of the added organic solvent was not obtained, but a measurement of what remained in the water phase. Control vials prepared exactly as the test vials were included in all experiments. These control vials were sterilized by autoclaving before adding the test chemical and analyzed periodically as were the test vials. By comparison of sterile and non-sterile (live) vials we determined if breakdown of the chemical occurred by hydrolysis or some other abiotic process.

All volatile halogenated organics in this study were analyzed by the purge and trap method (Ref. 35 and 36) using Tenax-GC and Carbopac C (0.1% SP-1000).

## C15 Initial Work with Tetrachloroethylene in Everglades Muck and Water (Test 1)

A one gallon sample of muck and a five gallon sample of surface water was collected on February 12, 1979. The muck sample with overlying water was kept in a loosely covered 5-gallon carboy to allow free exchange with the atmosphere. This initial muck and water combination was designated as Muck-Water 1.

In Test 1, we were still experimenting with several test systems in addition to the sealed vial method and used only tetrachloroethylene, 100 µg of which was injected into a 60 mL vial containing 10 mL screened muck and 50 mL surface water. Results of Test 1 with the sealed vial test are shown in Table 53 . The 100 g of tetrachloroethylene added to the vials contained other chlorinated impurities: 1.6 µg of trichloroethylene, a trace of trans- and cis- 1,2-dichloroethene, 0.13 g of methylene chloride and/or vinylidene chloride (these were not separated in our initial work), and 0.07 µg of vinyl chloride.

## TABLE 53

## TEST 1 - INITIAL WORK WITH TETRACHLOROETHYLENE IN EVERGLADES MUCK-WATER SAMPLE 1 IN SEALED VIALS

Approx. 100 μg of tetrachloroethylene per vial
μg in the water phase (based on total volume of muck and water)

| | tetrachloroethylene | | trichloroethylene | | cis 1,2-dichloroethene | | trans 1,2-dichloroethene | | methylene chloride and/or vinylidene chloride | | vinyl chloride | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | muck | control | muck | control | muck | control | muck | control | muck | control | muck | control |
| Initial Conc. | 87 | 94 | 1.1 | 1.2 | ND | ND | ND | ND | ND | ND | ND | ND |
| 7 days | 69 | 88 | 2.8 | 0.9 | 0.9 | ND | trace | ND | 0.02 | ND | trace | ND |
| 14 days | 47 | 83 | 3.1 | 1.0 | 2.1 | ND | 0.08 | ND | 0.05 | ND | 0.08 | ND |
| 21 days | 28 | 83 | 4.7 | 1.0 | 3.8 | ND | 0.11 | ND | 0.15 | ND | 1.7 | ND |

The muck initially adsorbed approximately 15 percent of the tetrachloroethylene leaving initial concentrations of 84 and 87 µg per vial in the water phase (Table 53).

A low concentration of trichloroethylene was detected initially, but none of the other chlorinated organic impurities of the tetrachloroethylene was found and apparently were adsorbed by the muck. In the sterilized control vials, no degradation of tetrachloroethylene, nor the small amount of trichloroethylene, was observed. In the muck vials, a consistent decrease was observed in the concentration of tetrachloroethylene with a consistent increase in the levels of lower chlorinated species.

Initial problems encountered using the sealed vial method were 1) maintaining sterility of the control vials and 2) designing a purging apparatus capable of handling viscous and foaming culture media.

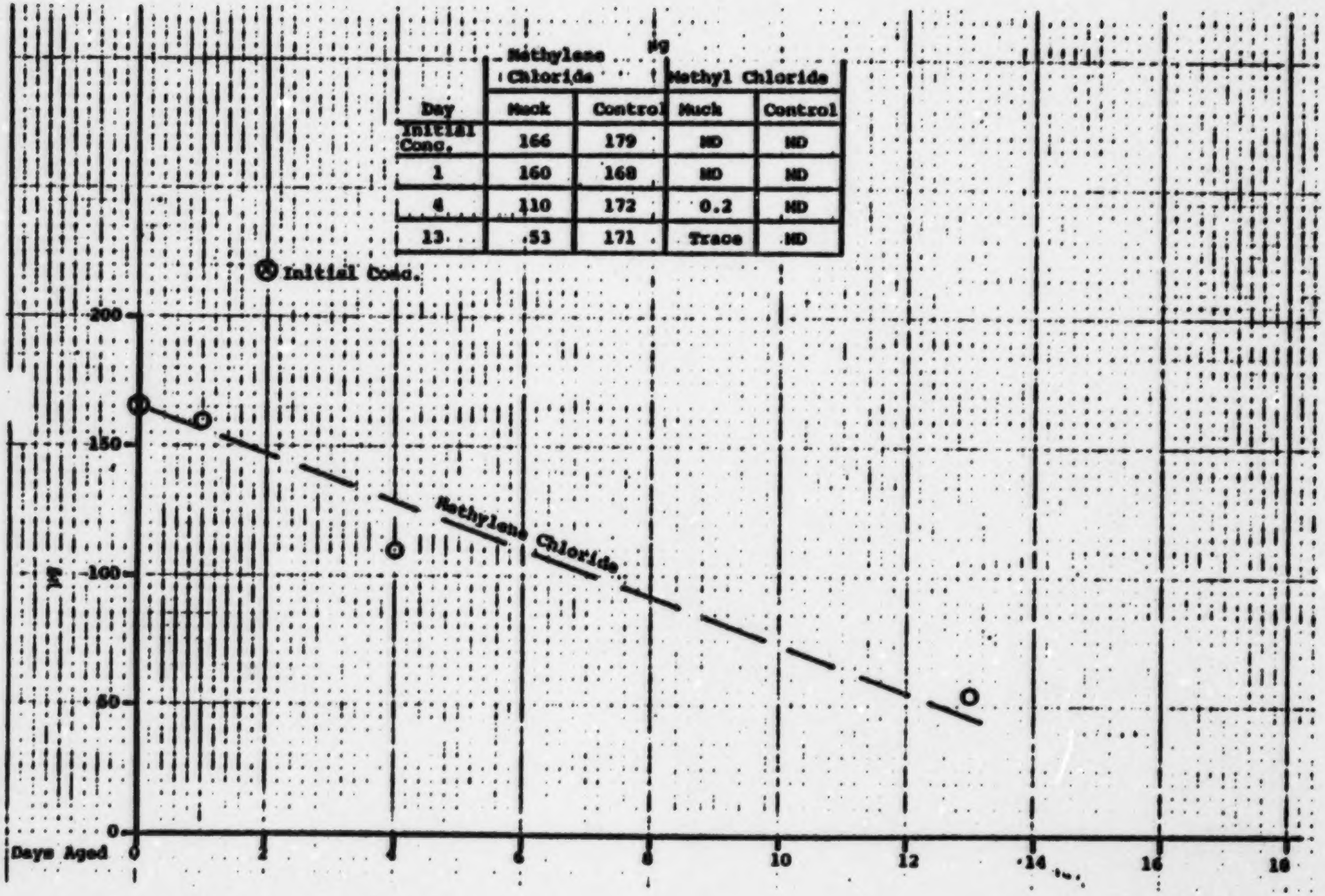
## C16 Biodegradation of Specific Compounds in Muck-Water Sample (Test 2)

As the results of Test 1 seemed to indicate that biodegradation of organic solvents could cause chloroethenes in raw water, similar tests were done with a wide range of chlorinated one and two-carbon compounds using the same muck-water sample. These experiments were designated as Test 2. During this time, biodegradation work in Muck-Water 1 was being carried on with most of the compounds shown in Table 51. We observed that all these preliminary data on decay rate appeared to be linear in a rectangular plot of concentration against time. It is not known if this linear relationship applies for a wide range in concentration and long aging times. Our work has been limited to a narrow low concentration range (50 to 500 g per 60 ml vial, usually 200 µg) and short aging times (7 to 30 days - usually 15 days). It is possible that short segments of any nonlinear decay curve might appear linear.

### C161 Chlorinated Methane Results (Test 2)

#### 1) Methylene Chloride

The decay rate of methylene chloride is shown in Figure 77 with the addition of approximately 200 µg of compound, the muck once again adsorbed approximately 17 percent resulting in an initial concentration of 166 µg. There was no change in the concentration in the control vial. In the muck vial, methylene chloride exhibited a steady decay rate and the chromatograms showed small levels of methyl chloride growth, varying from trace amounts to approximately 0.2 µg. The original sample of methylene chloride had no methyl chloride present.



|  | μg |  |  |  |
|---|---|---|---|---|
|  | Methylene Chloride |  | Methyl Chloride |  |
| Day | Muck | Control | Muck | Control |
| Initial Conc. | 166 | 179 | ND | ND |
| 1 | 160 | 168 | ND | ND |
| 4 | 110 | 172 | 0.2 | ND |
| 13 | 53 | 171 | Trace | ND |

Figure 77 Decay of methylene chloride (200 μg added to sealed vial) in Muck-Water Sample #1. (Test 2)

### 2) Chloroform

The decay rate of chloroform is shown in Figure 78. There was no decay in the control vial. In addition to chloroform decay in the muck vial, we also observed growth of methylene chloride. Methylene chloride development may have reached a peak, followed by a decline indicating further biodegradation. No methyl chloride growth was detected.

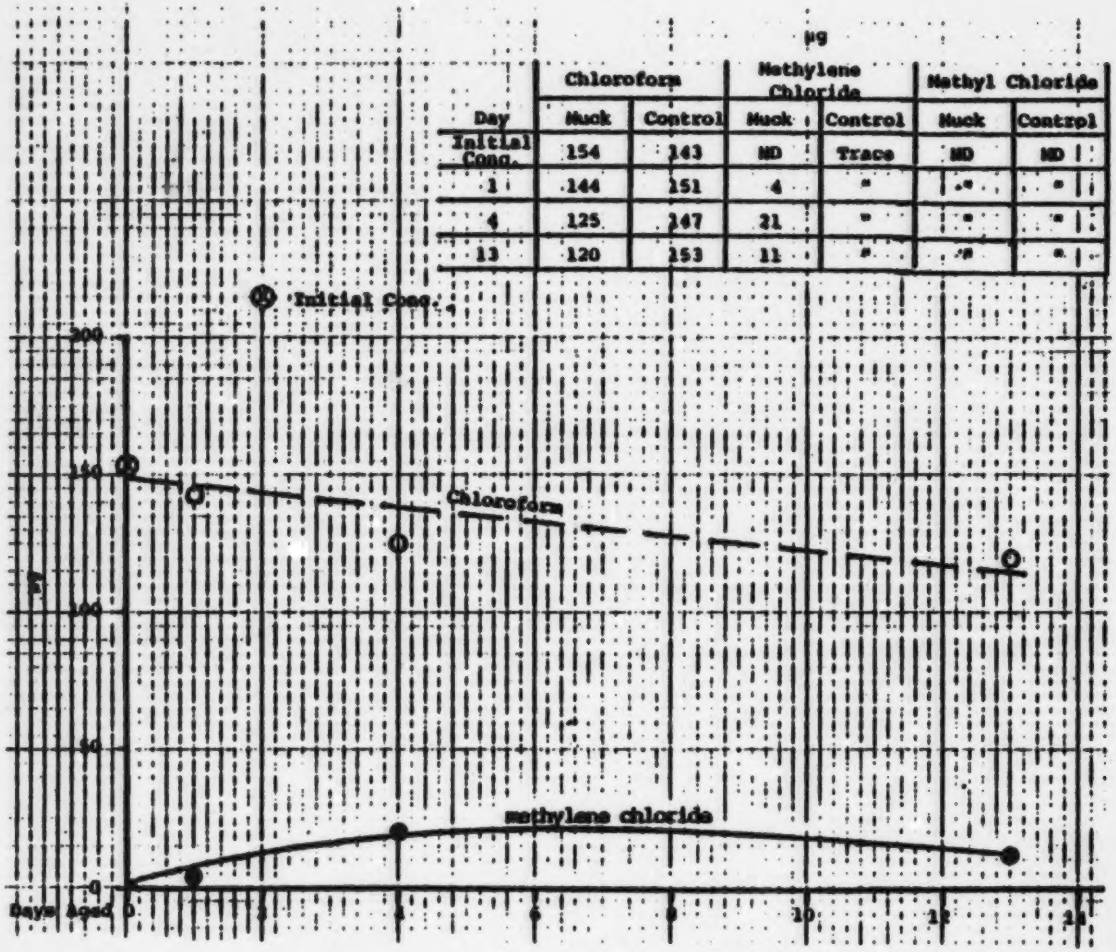
### 3) Carbon Tetrachloride

The decay rate of carbon tetrachloride is shown in Figure 79. The initial sample of carbon tetrachloride had a small level of chloroform and methylene chloride as impurities, seen in the initial concentration in the control vial. Accompanying the decay of carbon tetrachloride, was the growth of chloroform and methylene chloride. From the growth data, there was at least a hint of a peak in both growth curves followed by a decline.

### 4) Tentative Conclusions on Biodegradation of Chloromethanes

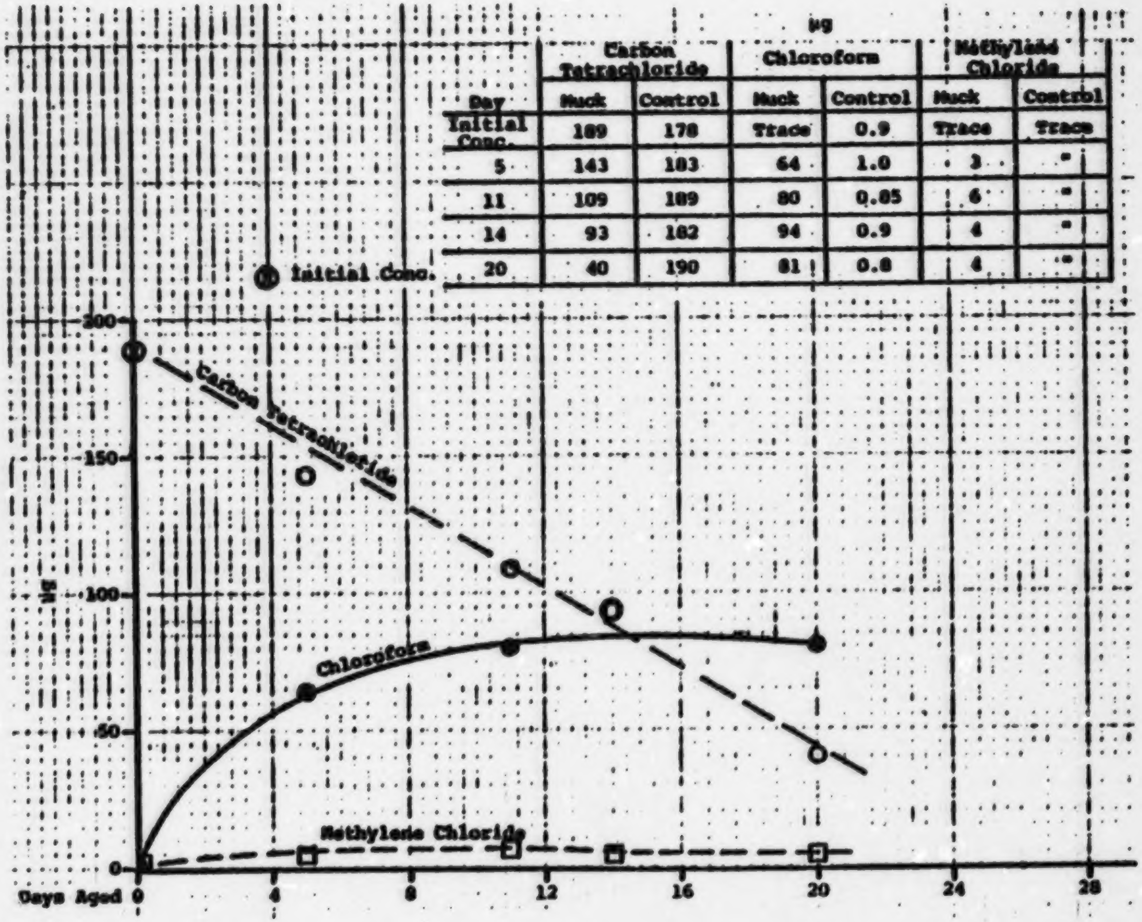
Before the biodegradation rates for the three compounds in Figures 77, 78 and 79 could be compared with each other, or with other compounds described later in this report, a common method of comparison had to be devised. Each compound tested might not be adsorbed to the same degree by the muck. Also it was difficult to add exactly the same number of micrograms of each substance to each vial, particularly when the levels of impurities in each substance varied. The decay and growth of chlorinated organics was determined only in the water phase, but the calculations were based on the total volume of muck and water phases. It was not known how the compounds adsorbed by the muck might exchange with the water phase. Of the compounds studied, initial adsorption by the muck varied from 6% to 18%, averaging 12%. If the compounds were treated in the same way, relative comparison of results could be made despite this variability as error of + 15% would not materially affect conclusions. The following approach of handling the data was used:

In Figures 77, 78 and 79 the best-fit decay lines extended to the X-axis was used to indicate the time for complete decay for the initial concentration of each compound. Dividing the initial concentration in μg by the time for complete decay in days gave the slope of the decay line. Both of these values are shown in Table 54. Using the slope values, the decay time for each compound at a common initial concentration (200 μg was chosen) was calculated. These values are shown in Table 54.



|  | μg |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | Chloroform |  | Methylene Chloride |  | Methyl Chloride |  |
| Day | Muck | Control | Muck | Control | Muck | Control |
| Initial Conc. | 154 | 143 | ND | Trace | ND | ND |
| 1 | 144 | 151 | 4 | " | " | " |
| 4 | 125 | 147 | 21 | " | " | " |
| 13 | 120 | 153 | 11 | " | " | " |

Figure 78 Decay of chloroform (200 μg added to sealed vial) in Muck-Water Sample #10 (Test 2).



| | µg | | | | | |
|---|---|---|---|---|---|---|
| | Carbon Tetrachloride | | Chloroform | | Methylene Chloride | |
| Day | Muck | Control | Muck | Control | Muck | Control |
| Initial Conc. | 189 | 178 | Trace | 0.9 | Trace | Trace |
| 5 | 143 | 183 | 64 | 1.0 | 3 | " |
| 11 | 109 | 189 | 80 | 0.85 | 6 | " |
| 14 | 93 | 182 | 94 | 0.9 | 4 | " |
| 20 | 40 | 190 | 81 | 0.8 | 4 | " |

Figure 79 Decay of carbon tetrachloride (200 µg added to sealed vial) in Muck-Water Sample #1 (Test 2).

## TABLE 54

## DECAY RATE DATA FOR CHLOROMETHANES IN MOCK-WATER SAMPLE 1 (TEST 2)

| | Days For Complete Decay (Based on Initial Conc. for each CPD.) | Slope of Best-fit Decay Curve | Days for Complete Decay of (200 μg of cpd.) | Half-Life in Days (200 μg of cpd.) |
|---|---|---|---|---|
| methylene chloride | 18 | 9.2 | 21.7 | 10.9 |
| chloroform | 54 | 2.8 | 54 | 35.7 |
| carbon tetrachloride | 26 | 7.3 | 26 | 13.7 |
| methyl chloride | <18* | >9.2* | <21.7* | <10.9* |

*estimated

The half-life values for the common initial concentration of 200 μg is also shown. This procedure of treating the data was followed throughout this report.

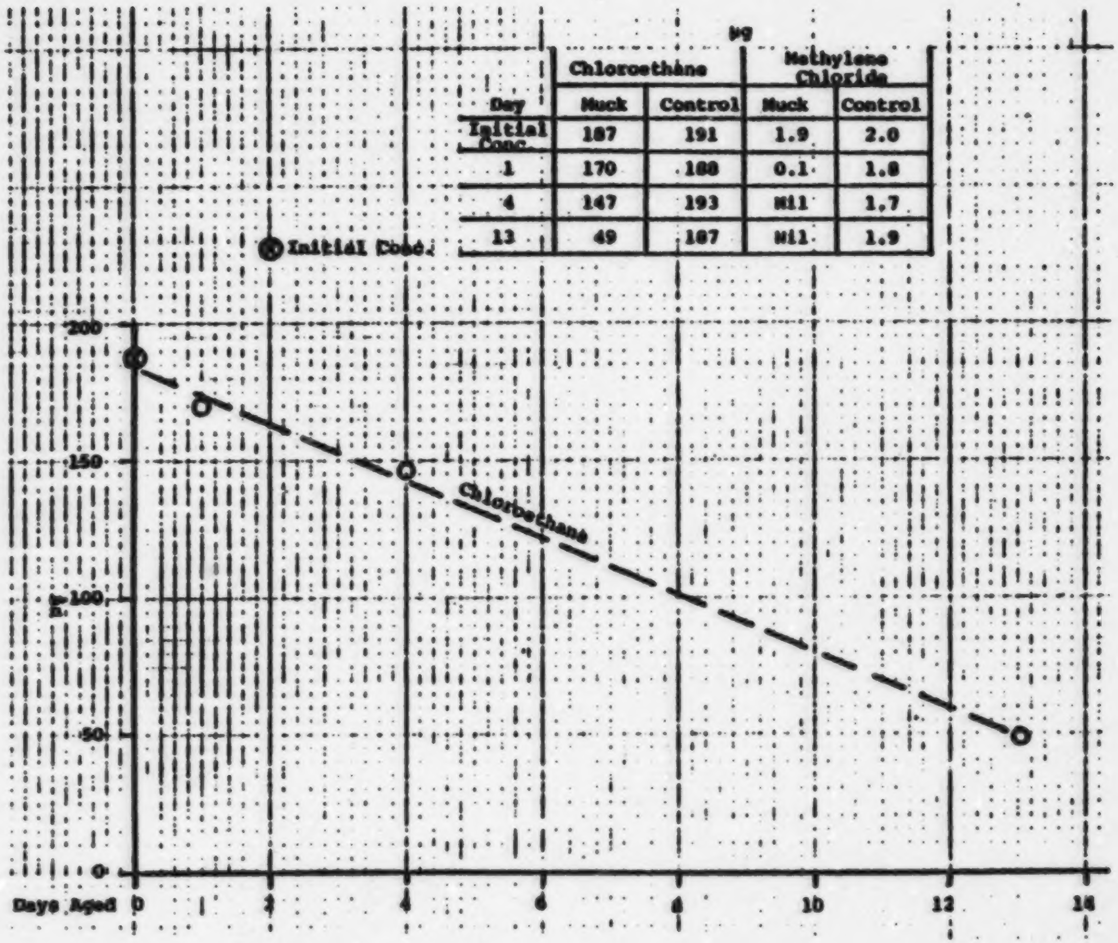
While the decay rate values in Table 54 are understood to be preliminary and approximations for the particular system, they do explain a great deal about the growth of lower chlorinated compounds and their subsequent decay. For example, in Figure 79, the large growth of chloroform observed might be accepted since the degradation rate of chloroform was much slower than for carbon tetrachloride. One might also accept the possibility that a growth curve might peak and then decay, because as the precursor (higher molecular weight chlorinated compound) decays, the rate of growth of the by-product should decrease.

The low level of methylene chloride growth appears to be consistent with its decay rate (faster than carbon tetrachloride or chloroform). From these data, one might be able to infer something about the decay rate of methyl chloride, even though it was not actually tested. As very low level growth of methyl chloride was observed, as higher precursors decayed, one might then assume that its decay rate might be faster than that of methylene chloride. This explains the estimated results for methylene chloride shown in Table 54.

### C162 Chlorinated Ethane Results (Test 2)

### 1) Chloroethane

The decay rate of chloroethane is shown in Figure 80. The straight decay line projected to the "X" axis indicated 18 days for complete decay of the



|  | µg |  |  |  |
|---|---|---|---|---|
|  | Chloroethane |  | Methylene Chloride |  |
| Day | Muck | Control | Muck | Control |
| Initial Conc. | 187 | 191 | 1.9 | 2.0 |
| 1 | 170 | 188 | 0.1 | 1.8 |
| 4 | 147 | 193 | Nil | 1.7 |
| 13 | 49 | 187 | Nil | 1.9 |

Figure 80 Decay of chloroethane (200 µg added to sealed vial) in Muck-Water Sample #1 (Test 2).

initial concentration of 187 μg. The initial sample of chloroethane contained approximately 2.0 μg of methylene chloride, which also exhibited decay.

### 2) 1,1-Dichloroethane

The plot of data in Figure 81 indicated no biodegradation of 1,1-dichloroethane in 14 days in our system. The initial sample of 1,1-dichloroethane (approximately 200 μg) contained approximately 6 μg of other chlorinated compounds, most of which was chloroethane. Most of the remainder was methylene chloride. The concentration of methylene chloride and chloroethane in the muck vial did not show the expected rate of decay (it was slower than expected) so a small increase of these two compounds could have resulted from some 1,1-dichloroethane decay. The amount of decay was probably too small to detect by the analytical method used.

### 3) 1,2-Dichloroethane

The data in Figure 82 indicated no decay of 1,2-dichloroethane in 14 days. A small amount of methylene chloride impurity in the initial sample (approximately 2 μg in the 200 μg sample) was the major lower molecular weight compound and it was completely biodegraded.

### 4) 1,1,1-Trichloroethane

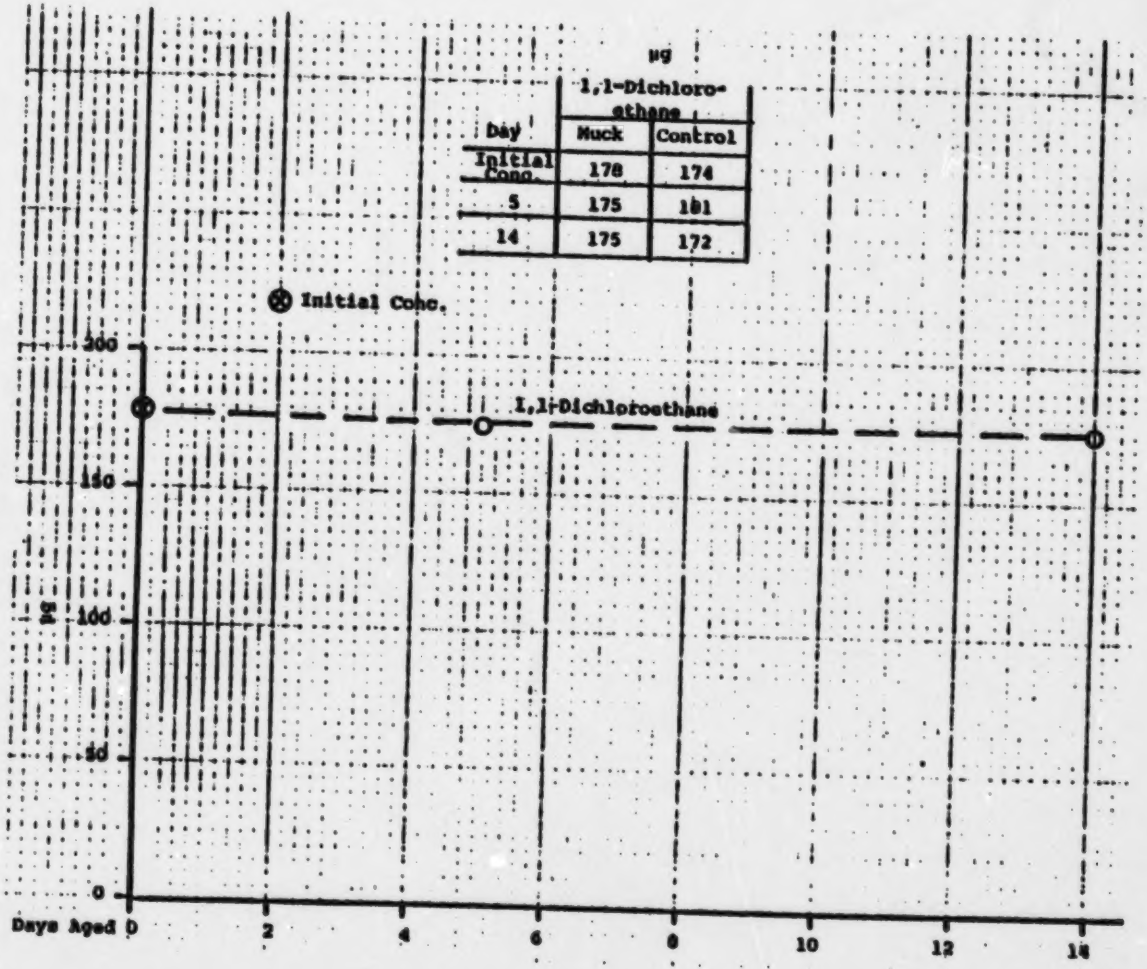
The available sample of 1,1,1-trichloroethane contained many chlorinated impurities. In this preliminary work, GC/MS was not used for confirmation of chlorinated compound peaks. Standards were run for GC peaks. With this in mind, it was reported that the initial 200 μg of 1,1,1-trichloroethane contained the following:

28 μg methylene chloride
18 μg 1,1,2-trichloroethane
unknown amount 1,2-dichloroethane
small amounts of unidentified chlorinated compounds
no 1,1-dichloroethane

With the above mixture, a mass balance of aged results was not possible. Because of the high level of impurities, approximately 250 μg of the compound was added to the test vial to have an approximate initial concentration of 200 μg of 1,1,1-trichloroethane. As shown in Figure 83, 1,1,1-trichloroethane appeared to decay at a fairly rapid rate. Complete decay for the initial concentration of 186 μg was estimated at 29 days. An increase of 1,1-dichloroethane was observed.

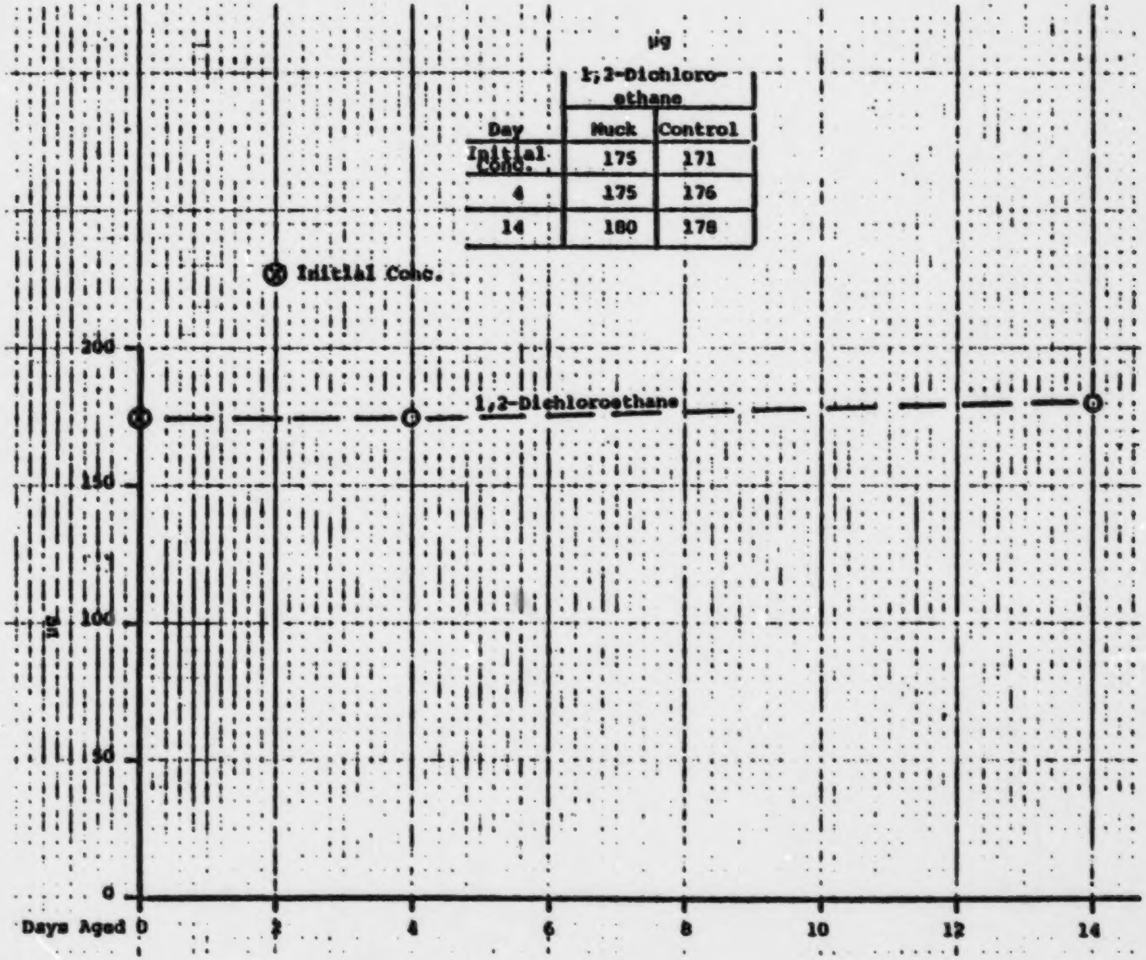
### 5) 1,1,2-Trichloroethane

The available sample of 1,1,2-trichloroethane was also contaminated with other chlorinated compounds. The initial 200 μg contained approximately 60 μg of impurities, approximately one-third of which was 1,2-dichloroethane. Only a small amount of methylene chloride was present. Again, approximately 250 μg



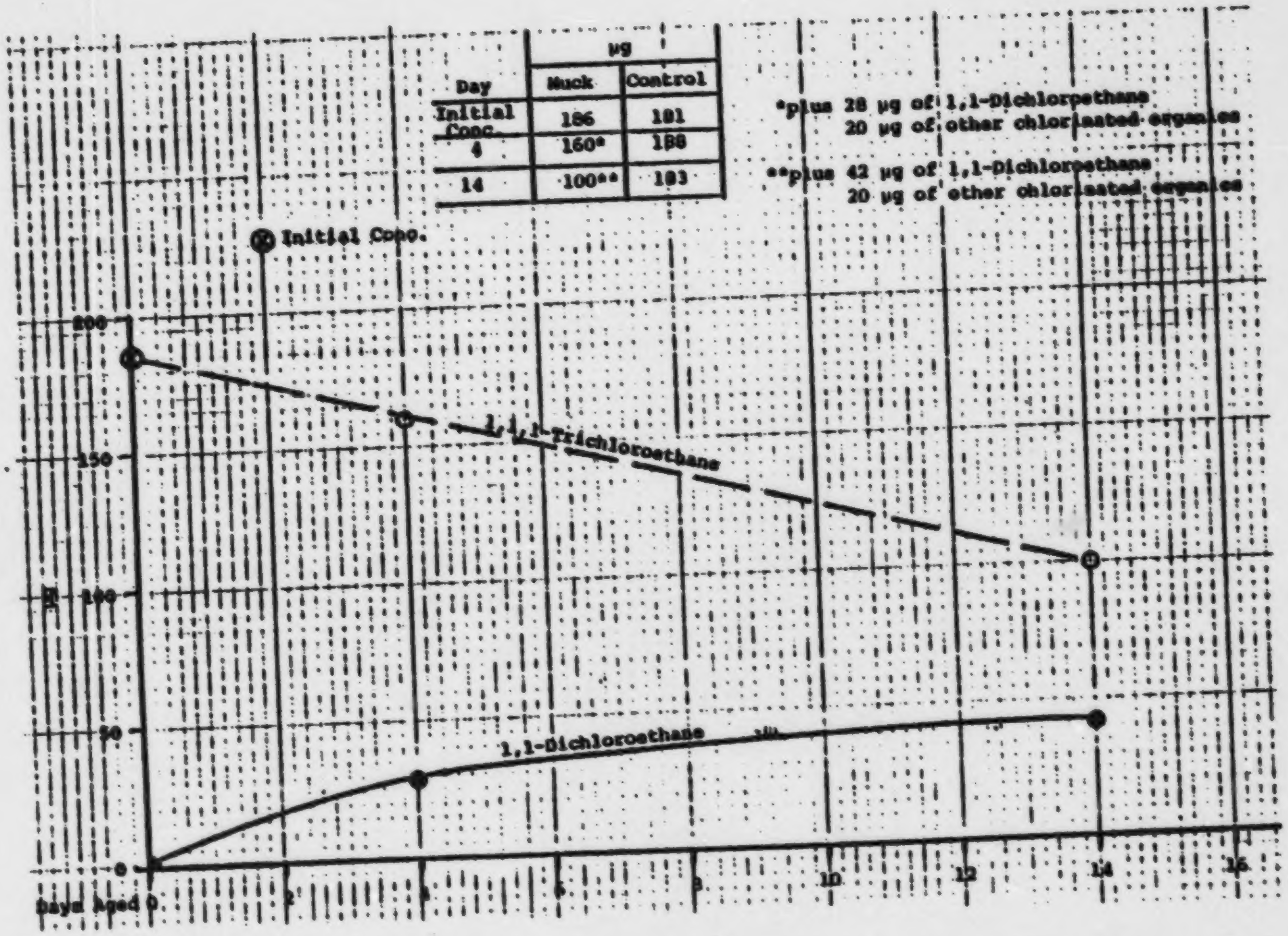
| Day | µg<br>1,1-Dichloroethane<br>Muck | <br><br>Control |
|---|---|---|
| Initial Conc. | 178 | 174 |
| 5 | 175 | 181 |
| 14 | 175 | 172 |

Figure 81 Decay of 1,1-dichloroethane (200 µg added to sealed vial) in Muck-Water Sample #1 (Test 2).



| Day | 1,2-Dichloroethane | |
|---|---|---|
| | Muck | Control |
| Initial Conc. | 175 | 171 |
| 4 | 175 | 176 |
| 14 | 180 | 178 |

Figure 82 Decay of 1,2-dichloroethane (200 µg added to sealed vial) in Muck-Water Sample #1 (Test 2).



| Day | μg Muck | μg Control |
|---|---|---|
| Initial Conc. | 186 | 181 |
| 4 | 160* | 188 |
| 14 | 100** | 183 |

*plus 28 μg of 1,1-Dichloroethane
20 μg of other chlorinated organics

**plus 42 μg of 1,1-Dichloroethane
20 μg of other chlorinated organics

Figure 83 Decay of 1,1,1-trichloroethane (200 μg added to sealed vial) in Muck-Water Sample #1 (Test 2).

of the mixture was added to the test vial to begin the test with approximately 200 μg of 1,1,2-trichloroethane. As shown in Figure 84 a fairly rapid decay rate for 1,1,2-trichloroethane was seen. Time for complete decay for the initial concentration of 199 g was estimated at 48 days. An increase in 1,2-dichloroethane was observed.

### 6) Tentative Conclusions on Biodegradation of Chloroethanes

Conclusions based on the data for chloroethanes must be reserved; however, it might be said that chloroethane, 1,1,1-trichloroethane and 1,1,2-trichlor oethane exhibit fairly rapid rates of decay as shown in Table 55.

TABLE 55

DECAY RATE DATA FOR CHLOROETHANES
IN MOCK-WATER SAMPLE #1 (TEST 2)

| | Days for Complete Decay (Based on Initial Conc. For Each CPD) | Slope of Best-fit Decay Curve | Days for Complete Decay of 200 μg of cpd. | Half-Life in Days (200 μg of cpd. |
|---|---|---|---|---|
| chloroethane | 18 | 10.39 | 19.3 | 9.6 |
| 1,1-trichloroethane | 29 | 6.41 | 31.2 | 15.6 |
| 1,2-trichloroethane | 48 | 4.15 | 48 | 24.1 |
| 1-dichloroethane | no decay in 14 days | | | no decay in 14 days |
| 2-dichloroethane | no decay in 14 days | | | no decay in 14 days |

1,1-dichloroethane and 1,2-dichloroethane may have very low decay rates, exhibiting no decay in 14 days.

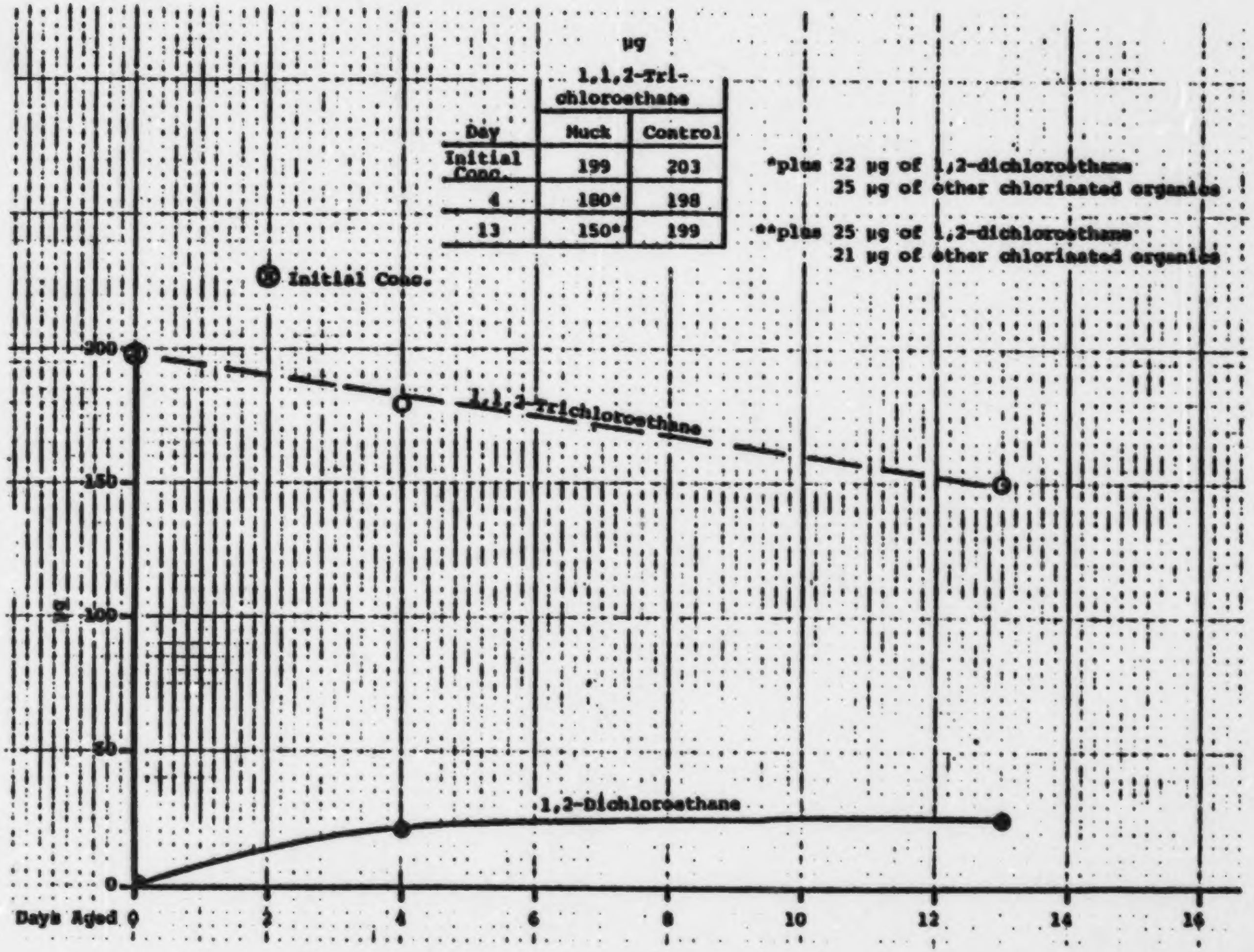
## C163 Chlorinated Ethene Results (Test 2)

### 1) Vinyl Chloride

For what later seemed no sound reasoning, it was decided to inject only 20 μg instead of the usual 200 μg. Figure 85 indicated that vinyl chloride did not decay in 17 days.

### 2) Vinylidene Chloride

Vinylidene chloride exhibited some decay as shown in Figure 86, with

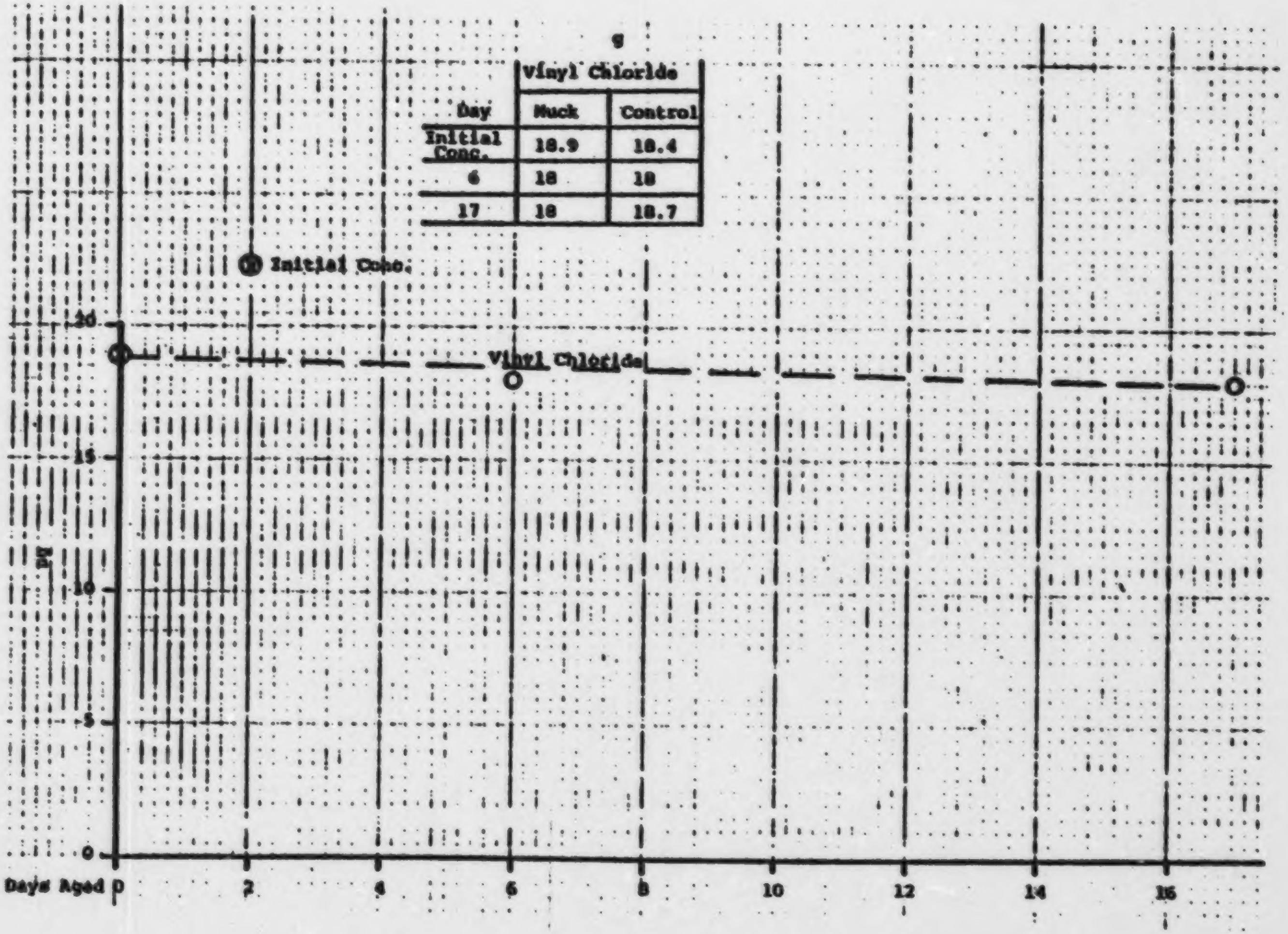


|  | µg |  |
|---|---|---|
|  | 1,1,2-Trichloroethane |  |
| Day | Muck | Control |
| Initial Conc. | 199 | 203 |
| 4 | 180* | 198 |
| 13 | 150** | 199 |

*plus 22 µg of 1,2-dichloroethane
25 µg of other chlorinated organics

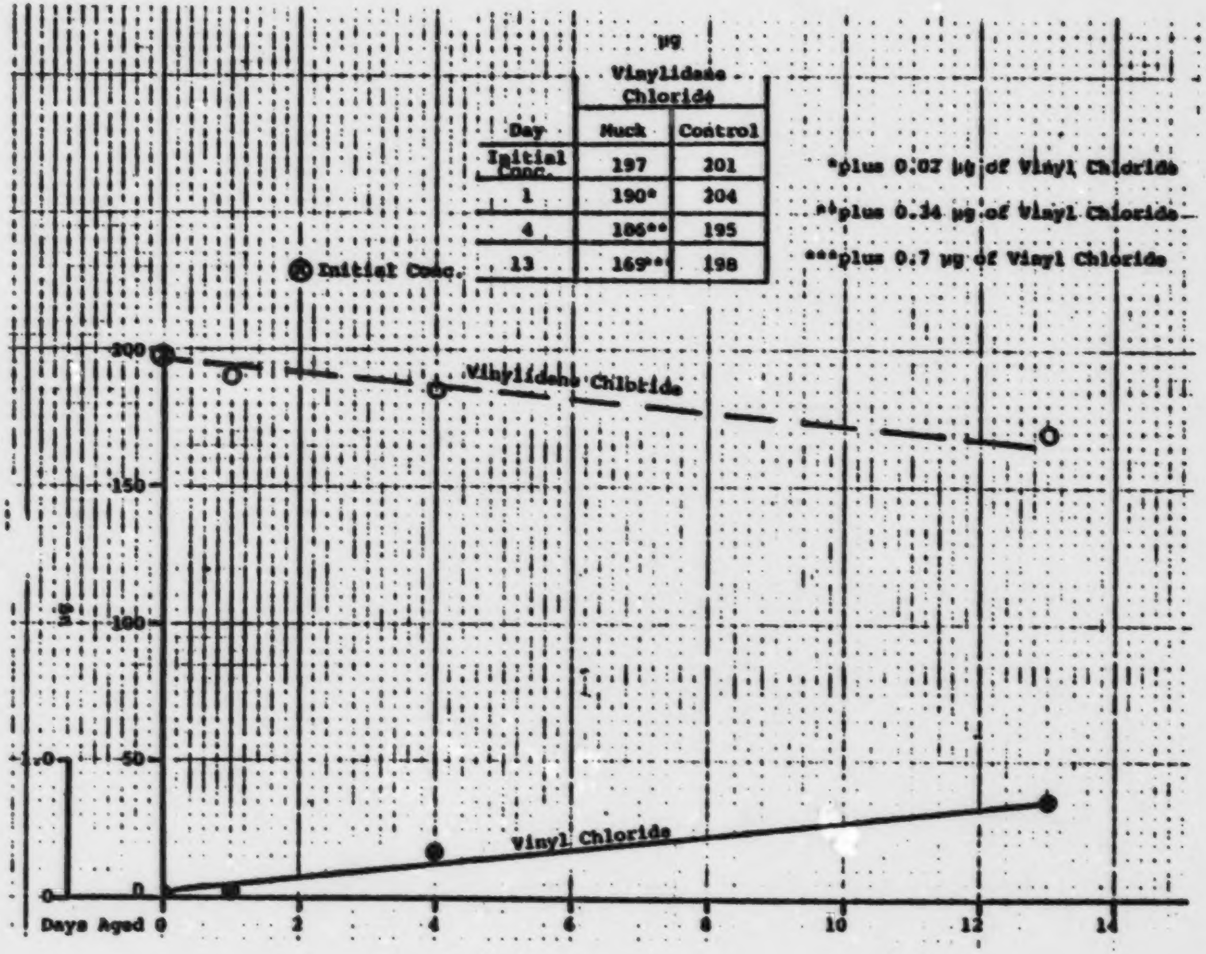
**plus 25 µg of 1,2-dichloroethane
21 µg of other chlorinated organics

Figure 84 Decay of 1,1,2-trichloroethane (200 µg added to sealed vial) in Muck-Water Sample #1 (Test 2).



|  | Vinyl Chloride |  |
|---|---|---|
| Day | Muck | Control |
| Initial Conc. | 18.9 | 18.4 |
| 6 | 18 | 18 |
| 17 | 18 | 18.7 |

Figure 85 Decay of vinyl chloride (20 µg added to sealed vial) in Muck-Water Sample #1 (Test 2).



| Day | μg Vinylidene Chloride Muck | μg Vinylidene Chloride Control |
|---|---|---|
| Initial Conc. | 197 | 201 |
| 1 | 190* | 204 |
| 4 | 186** | 195 |
| 13 | 169*** | 198 |

*plus 0.02 μg of Vinyl Chloride

**plus 0.34 μg of Vinyl Chloride

***plus 0.7 μg of Vinyl Chloride

Figure 86 Decay of vinylidene chloride (200 μg added to sealed vial) in Muck-Water Sample #1 (Test 2).

production of a small amount of vinyl chloride (note the separate "Y" axis scale for vinyl chloride). If methylene chloride was also a by-product, the decay rate for vinylidene chloride might be somewhat faster because at this phase of the work we were still not separating methylene chloride and vinylidene on the GC.

### 3) Trans-1,2-dichloroethene

The 200 μg sample of the available trans-1,2-dichloroethene contained 0.8 μg of trichloroethylene, 0.5 μg of cis-1,2-dichloroethene, 0.03 μg of tetrachloroethylene, 0.3 μg of methylene chloride and/or vinylidene chloride and no vinyl chloride. As shown in Figure 87, it was observed that essentially no decay of trans-1,2-dichloroethene occurred in 20 days. However, a small growth of vinyl chloride was observed, which could have come from the starting compound and/or from other chloroethene impurities.

### 4) Cis-1,2-dichloroethene

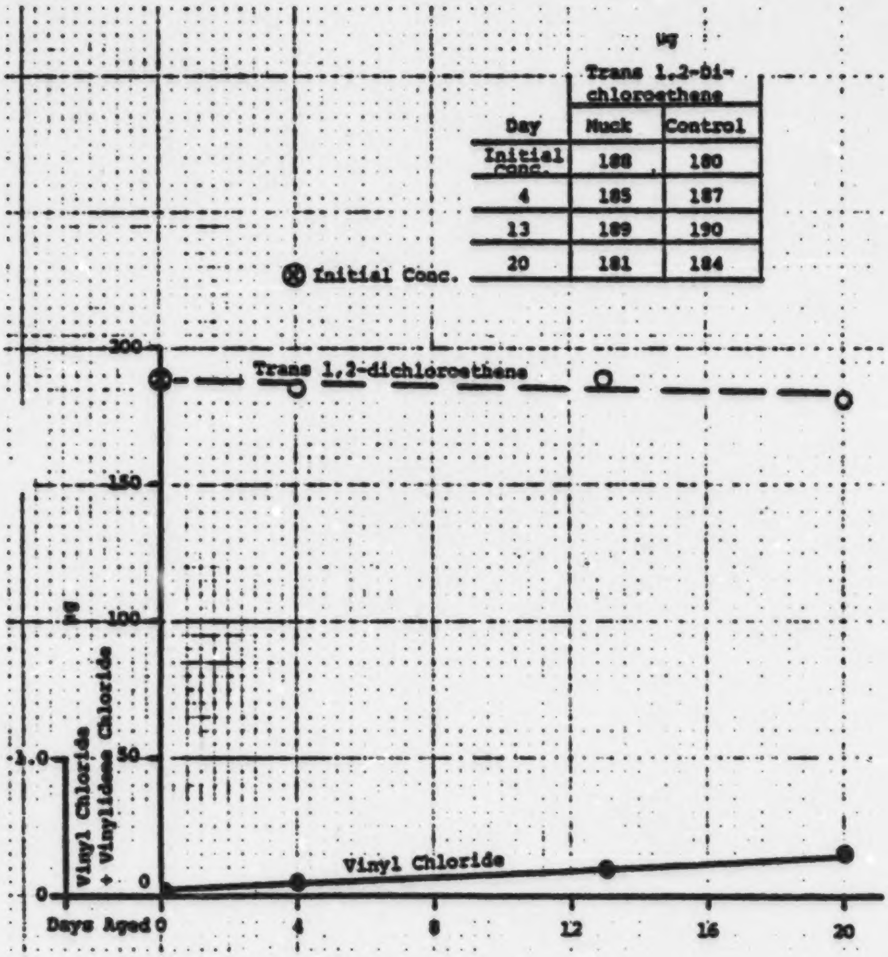
The initial 200 μg sample of cis-1,2-dichloroethene contained 11 μg of trans 12-dichloroethene, 2.2 μg of trichloroethylene and no vinyl chloride. No decay was observed for cis-1, 2-dichloroethene, Figure 88. However, the small amount of trichloroethylene showed decay starting at 2.2 μg as impurity and decreasing to 0.17 μg in 20 days. There was growth of vinyl chloride and the methylene chloride and/or vinylidene chloride peak, some of which would have come from the trichloroethylene present.

### 5) Trichloroethylene

The 200 μg sample of trichloroethylene contained 0.02 μg of vinyl chloride, 0.05 μg of methylene chloride and/or vinylidene chloride and no trans-or cis-1,2-dichloroethene. A fairly rapid decay rate for trichloroethylene was indicated by Figure 89. On a separate "Y" axis scale, the growth of vinyl chloride, methylene chloride and/or vinylidene chloride and trans and cis 1,2-dichloroethene is apparent. Complete decay of trichloroethylene (200 μg) would probably occur in 76 days.

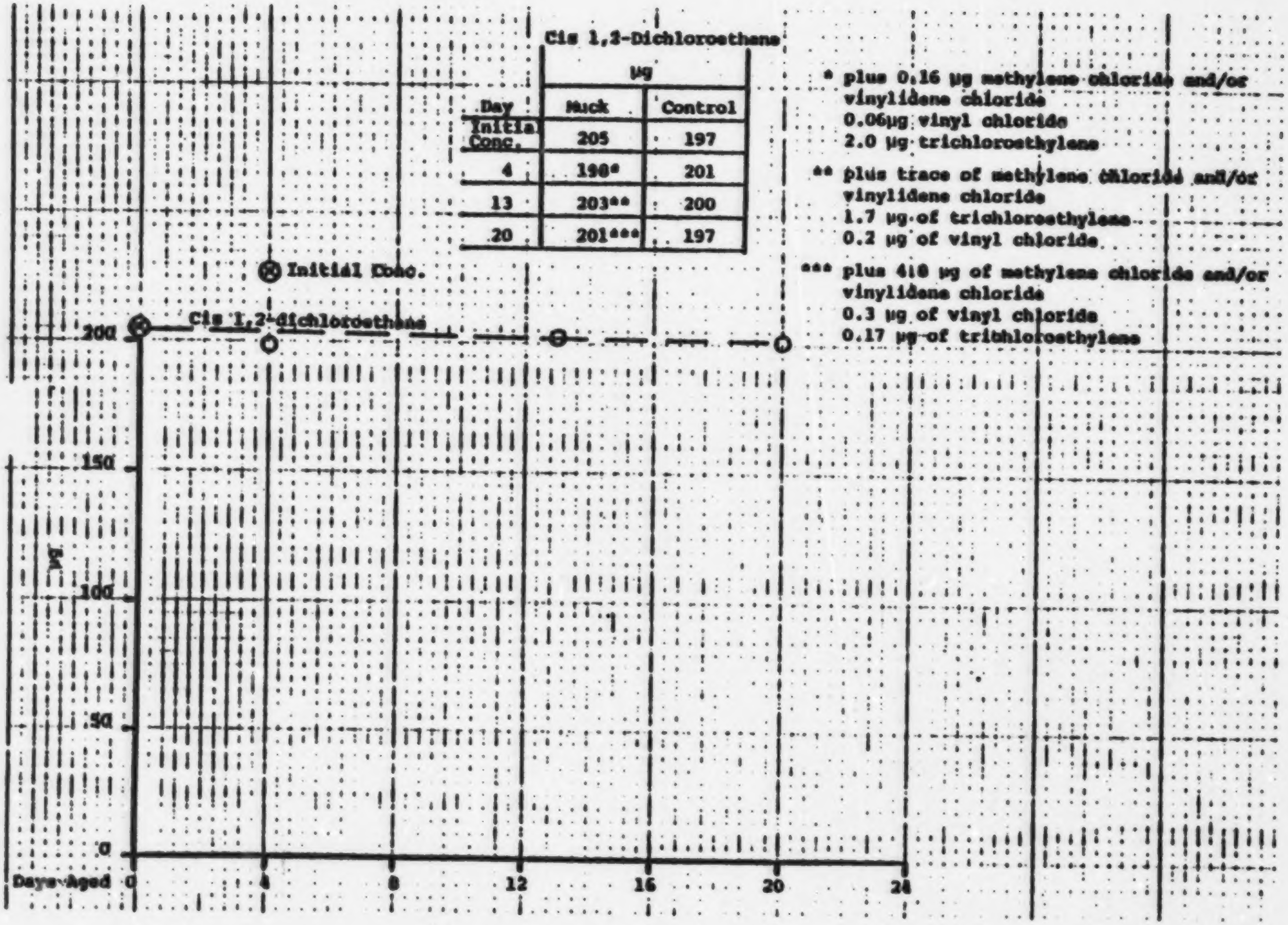
### 6) Tetrachloroethylene

The sample of 200 μg of tetrachloroethylene contained 3.7 μg of trichloroethylene, a trace of trans-and cis-1,2-dichloroethene, 0.32 μg of methylene chloride and/or vinylidene chloride and 0.1 μg of vinyl chloride. The decay rate of tetrachloroethylene is shown in Figure 90. The estimated time to complete decay for 200 μg appeared to be approximately 70 days. The decay rate of tetrachloroethylene in Test 1, Table 53 was also plotted in Figure 90, and the slope of the decay line was very close to the slope of the line in Test 2. The growth of trichloroethylene, trans-and cis-1,2-dichloroethene, methylene chloride and/or vinylidene chloride, and vinyl chloride is also shown in Figure 90.



| | μg<br>Trans 1,2-di-chloroethene | |
|---|---|---|
| Day | Muck | Control |
| Initial conc. | 188 | 180 |
| 4 | 185 | 187 |
| 13 | 189 | 190 |
| 20 | 181 | 184 |

Figure 87 Decay of trans 1,2-dichloroethene (200 μg added to sealed vial) in Muck-Water Sample #1 (Test 2).



Cis 1,2-Dichloroethene

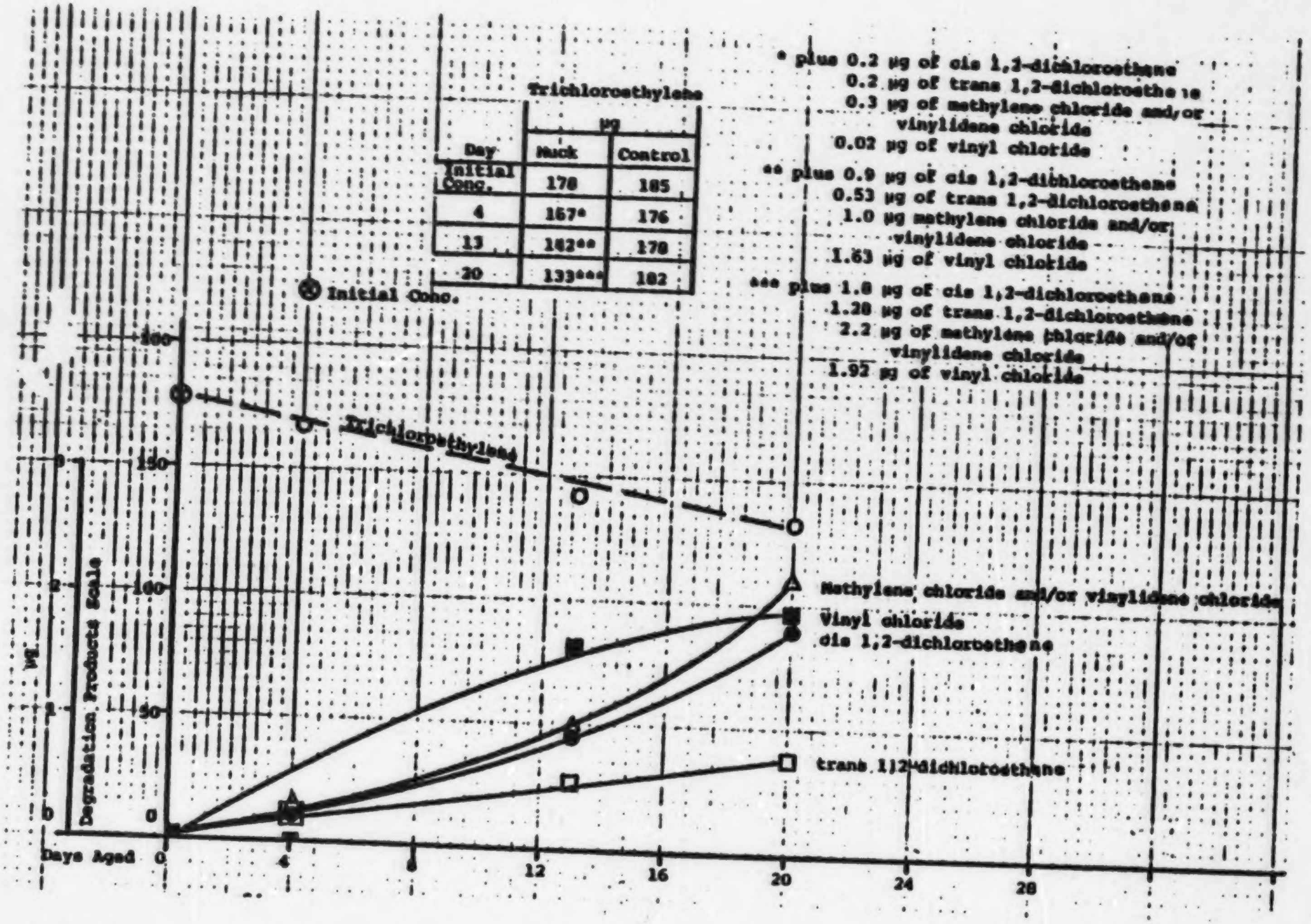
| Day | µg |  |
|---|---|---|
|  | Muck | Control |
| Initial Conc. | 205 | 197 |
| 4 | 198* | 201 |
| 13 | 203** | 200 |
| 20 | 201*** | 197 |

* plus 0.16 µg methylene chloride and/or vinylidene chloride
0.06µg vinyl chloride
2.0 µg trichloroethylene

** plus trace of methylene chloride and/or vinylidene chloride
1.7 µg of trichloroethylene
0.2 µg of vinyl chloride

*** plus 4.8 µg of methylene chloride and/or vinylidene chloride
0.3 µg of vinyl chloride
0.17 µg of trichloroethylene

Figure 88 Decay of Cis 1,2-dichloroethene (200 µg in sealed vial) in Muck-Water Sample #1 (Test 2)



Trichloroethylene

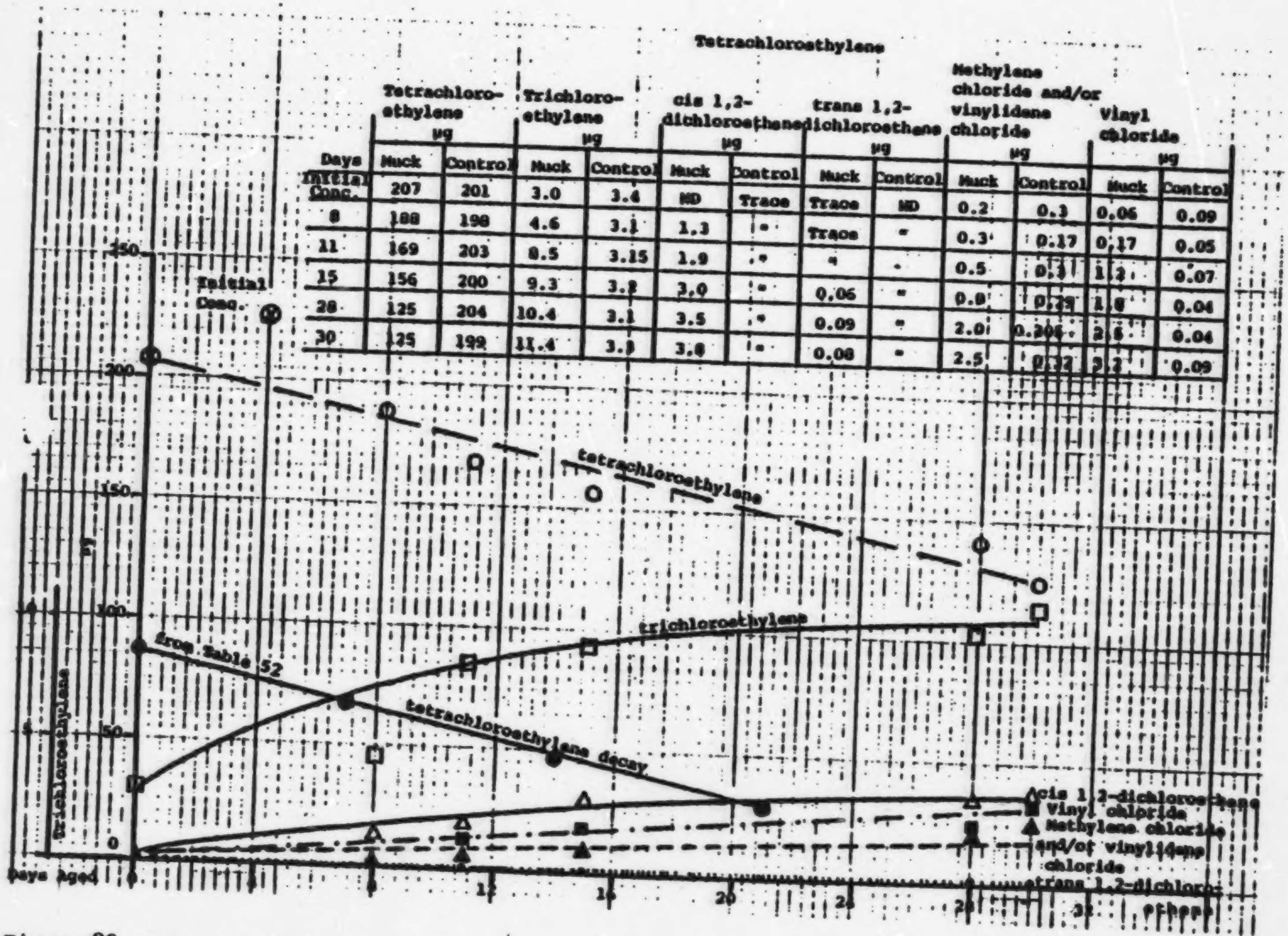
| Day | µg Muck | µg Control |
|---|---|---|
| Initial Conc. | 178 | 185 |
| 4 | 167* | 176 |
| 13 | 182** | 178 |
| 20 | 133*** | 182 |

* plus 0.2 µg of cis 1,2-dichloroethene
0.2 µg of trans 1,2-dichloroethene
0.3 µg of methylene chloride and/or vinylidene chloride
0.02 µg of vinyl chloride

** plus 0.9 µg of cis 1,2-dichloroethene
0.53 µg of trans 1,2-dichloroethene
1.0 µg methylene chloride and/or vinylidene chloride
1.63 µg of vinyl chloride

*** plus 1.8 µg of cis 1,2-dichloroethene
1.28 µg of trans 1,2-dichloroethene
2.2 µg of methylene chloride and/or vinylidene chloride
1.92 µg of vinyl chloride

Figure 89 Decay of trichloroethylene (200 µg in sealed vial) in Muck-Water Sample #1 (Test 2)



| Days | Tetrachloroethylene µg | | Trichloroethylene µg | | cis 1,2-dichloroethene µg | | trans 1,2-dichloroethene µg | | Methylene chloride and/or vinylidene chloride µg | | Vinyl chloride µg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Muck | Control | Muck | Control | Muck | Control | Muck | Control | Muck | Control | Muck | Control |
| Initial Conc. | 207 | 201 | 3.0 | 3.4 | ND | Trace | Trace | ND | 0.2 | 0.3 | 0.06 | 0.09 |
| 8 | 188 | 198 | 4.6 | 3.1 | 1.3 | - | Trace | - | 0.3 | 0.17 | 0.17 | 0.05 |
| 11 | 169 | 203 | 8.5 | 3.15 | 1.9 | - | - | - | 0.5 | 0.3 | 1.2 | 0.07 |
| 15 | 156 | 200 | 9.3 | 3.2 | 3.0 | - | 0.06 | - | 0.8 | 0.29 | 1.8 | 0.04 |
| 28 | 125 | 204 | 10.4 | 3.1 | 3.5 | - | 0.09 | - | 2.0 | 0.206 | 2.6 | 0.04 |
| 30 | 125 | 199 | 11.4 | 3.1 | 3.8 | - | 0.08 | - | 2.5 | 0.32 | 3.2 | 0.09 |

Figure 90 Decay of tetrachloroethylene (200 µg added to sealed vial) in Muck-Water Sample #1 (Test 2).

7) Tentative conclusion on chloroethene biodegradation

Decay rates of all chloroethene compounds are summarized in Table 56.

Tetrachloroethylene biodegraded slightly faster than trichloroethylene, and both of these compounds degraded considerably faster than vinylidene chloride. Vinyl chloride, trans 1,2-dichloroethene and cis 1,2-dichloroethene showed no degradation in 18, 20 and 30 days, respectively.

## C164 Tentative Conclusions on Biodegradation of all Compounds (Test 2)

The biodegradation rates in Tables 54, 55 and 56 are presented in Table 57 to allow an overall comparison.

1) All members of the chloromethane family decayed fairly rapidly. The one-chlorine compound decayed fastest, followed by the two- and four chlorine compounds. The three-chlorine compound, chloroform, decayed the slowest in this family.

2) Of the five compounds studied in the chloroethane family, the one-chlorine compound decayed fastest, as in the chloromethane family. In fact, their decay rates, considering their half lives, were quite close, less than 10.9 days for methyl chloride and 9.6 days for chloroethane. The two isomers of the two-chlorine compounds showed no decay in the time period tested. The two isomers of the three-chlorine compounds, 1,1,1- and 1,1,2-trichloroethane, decayed quite rapidly with half lives of 15.6 and 24.1 days, respectively.

3) The decay rates for the chloroethene family were quite different from the chloromethane and chloroethane families. The one-chlorine compound, vinyl chloride, showed no degradation in the time period tested. Tetrachloroethylene and trichloroethylene degraded the fastest in this series with half lives of 33.8 and 42.7 days, respectively.

Vinylidene chloride degraded more slowly, having a half life of 52.9 days. The trans and cis isomers showed no degradation in the time period tested.

It is interesting to note that of the compounds exhibiting biodegradation in this study, the half life (based on 200 μg of compound) varied from a low of 9.6 days to a high of 52.9 days.

## C165 Using the Tentative Conclusions to Explain the Halogenated Organic Profile of Raw Water in Miami

Based on the biodegradation rates in Table 57 and the growth of by-products observed for each compound in this work, it seemed possible to

## TABLE 56

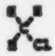
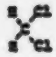
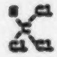
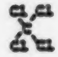
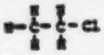
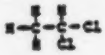
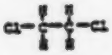
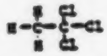
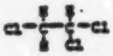
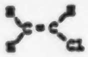
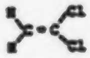
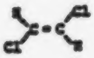
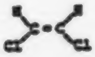
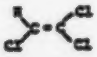
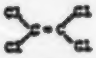
## DECAY RATE DATA FOR CHLOROETHENES IN MUCK-WATER SAMPLE #1 (TEST 2)

| | Days for complete decay (based on initial conc. of each compound) | Slope of Best-fit Decay Curve | Days for complete decay (approx. 200 µg compound) | Half Life in Days (200 µg cpd) |
|---|---|---|---|---|
| tetrachloroethylene | 70 | 2.96 | 67.6 | 33.8 |
| trichloroethylene | 76 | 2.34 | 85.4 | 42.7 |
| cis 1,2-dichloroethene | no decay in 30 days | no decay in 30 days | | |
| trans 1,2-dichloroethene | no decay in 20 days | no decay in 20 days | | |
| vinylidene chloride | 104 | 1.89 | 105.6 | 52.9 |
| vinyl chloride | no decay in 18 days | no decay in 18 days | | |

## TABLE 57

## BIODEGRADATION RATES FOR CHLOROMETHANE, CHLOROETHANE AND CHLOROETHENE FAMILIES OF COMPOUNDS

## (TEST 2, MUCK-WATER SAMPLE 1)

| Class | Compound | Molecular Structure | Slope of best-fit decay curve | Half-Life in Days (200 ug cpd) |
|---|---|---|---|---|
| chloromethanes | methyl chloride |  | >9.2 estimate | <10.9 |
| | methylene chloride |  | 9.2 | 10.9 |
| | chloroform |  | 2.8* | 35.7 |
| | carbon tetrachloride |  | 7.3 | 13.7 |
| chloroethanes | chloroethane |  | 10.39 | 9.6 |
| | 1,1-dichloroethane |  | small number | |
| | 1,2-dichloroethane |  | small number | |
| | 1,1,1-trichloroethane |  | 6.41 | 15.6 |
| | 1,1,2-trichloroethane |  | 4.15 | 24.1 |
| chloroethenes | vinyl chloride |  | small number | |
| | vinylidene chloride |  | 1.89 | 52.9 |
| | trans 1,2-dichloroethene |  | small number | |
| | cis 1,2-dichloroethene |  | small number | |
| | trichloroethylene |  | 2.34 | 42.7 |
| | tetrachloroethylene |  | 2.96 | 33.8 |

to combine the two and explain the halogenated organic profile of raw water as follows:

1) Methyl Chloride

Except in the case of a direct spill, one might expect to find very low levels of methyl chloride in raw water. Regardless of the precursor molecule, if it was formed by biodegradation, its biodegradation would be too fast for it to accumulate. Only trace amounts have ever been found in Miami raw water.

2) Methylene Chloride

When formed by biodegradation of a precursor molecule, one might expect that it would not accumulate to a very high level because of its fast degradation. More methylene chloride has been observed in raw water than methyl chloride, indicating that its decay rate is probably slower. In Table 48 a combined value of methylene chloride and/or vinylidene chloride was reported due to overlapping GC peaks. In some of the later work where these two compounds were separated by the GC, the indication was that probably most of the reported level for the sum of the two compound was actually due to vinylidene chlorlide. The average level of methylene chloride in raw water was probably less than 0.1 μg/L.

3) Chloroform and Carbon Tetrachloride

The only precursor molecule for chloroform, if formed by biodegradation would be carbon tetrachloride. As at most, only trace levels of carbon tetrachloride occur in Miami raw water, one would expect to find only trace levels of chloroform. Such was the case, when trace levels of chloroform were found, trace levels of bromodichloromethane and the chlorodibromomethane were also found suggesting that the source of the chloroform might be contamination by water that had been chlorinated.

4) Chloroethane

Chloroethane would be the chlorinated end product in the biodegradation of the whole family of chloroethanes. Regardless of the precursor, however, because of its rapid biodegradation rate one would expect to find only traces in raw water. Such was the case.

5) 1,1,1-Trichloroethane and 1,1,2-trichloroethane

If low levels of these two compounds entered the ground water, their biodegradation rate would probably be fast enough that one would only expect to find very low levels in raw water. 1,1,1-Trichloroethane, according to our work, decayed mainly to 1,1-dichloroethane, which has a long half life and therefore would probably be more likely observed in raw water. Also 1,1,2-trichloroethane decayed mainly to 1,2-dichloroethane, which also had a long half life and would also be more likely observed in raw water.

6) 1,1,-Dichloroethane and 1,2-Dichloroethane

If these compounds enter the water, they would probably persist for a long time as both have long half lives.

7) Vinyl Chloride

It is the final chlorinated biodegradation product of all higher molecular weight members of the chloroethene family and it had a long half life. Therefore, it should be quite common in water where higher members of the family were introduced. In fact, it was always observed in the two Miami well fields during the period of this work.

8) Vinylidene Chloride

As mentioned above, the GC peak assigned to methylene chloride and/or vinylidene chloride was mostly vinylidene chloride. It could result from the biodegradation of all higher members of the chloroethene family. Since it had a half life shorter than vinyl chloride, we would not expect it to be present in concentrations as high as vinyl chloride. In raw water it was usually less than one twentieth the concentration of vinyl chloride.

9) Trans and cis 1,2-Dichloroethene

Both compounds exhibited a long half life and both were produced by the biodegradation of tri- and tetrachloroethylene.

Although both have a long half life, the concentration of trans in our water was usually less than one twenty-fifth the concentration of cis. Apparently biodegradation favors the formation of cis. Half life then may not be the only factor in prediction what we might expect to find in raw water.

10) Tri- and Tetrachloroethylene

As the half life of both compounds is short, we would not expect to find either compound present in very high levels. This was the case in Miami raw water.

## C17 Identification of the Bacteria in Muck-Water 1

As the Everglades Muck-Water Sample 1 was biologically active on most of the chlorinated compounds studied in Test 2, an attempt was made to identify the bacteria present.

### C171 Identification Method

Aerobic and anaerobic mesophilic heterotrophic bacteria were isolated from mud used in biodegradation studies and from septum bottles containing mud, water, and organic solvents by the following technique:

### C1711 Mud and Water from Everglades

1) Duplicate sets of four plates of Standard Methods Agar (Ref. 10) and R2-A (Ref. 11) were made of dilutions of Everglades muck and water. One set of each dilution series was incubated aerobically at 35C; the other was incubated in BBL Gaspac disposable anaerobe bags at 35C.

2) All recognizably different colonies that were visible after 5 days were picked, streaked to isolate and purify, and subcultured under the same conditions in which they grew on primary culture.

3) Isolated colonies from the subcultures were picked for identification by the following techniques:

a. Gram, oxidase, and catalase reactions
b. (1) API 20E system (Analytab Division by Ayerst Laboratories, Plainview, NY) was used to help identify Gram-negative rods that grew aerobically.
   (2) Idenfification was based on API data bank information, Bergey's Manual, and the CDC mimeo taxonomy.
c. (1) API 20A system was used to help identify colonies that grew anaerobically.
   (2) Identification was based on the API data bank information and Bergey's Manual.
d. (1) API 20E system was used as a preliminary multi-test system for all other aerobes, but identification was based on Bergey's Manual and descriptions in the literature.

### C1712 Mud-Water Mixture from Test Septum Bottles

As the serum bottles were completely filled and contained reducible organic material, it was speculated that the bacteria would experience anaerobic conditions. It was further speculated that aerobic and microaerophilic bacteria could function under these conditions. Therefore, the same protocol was followed for each test bottle as for mud and water samples from the Everglades.

### C1713 Pure Culture Studies

1) Pure cultures of known strains (Difco Bactrol spp.) were grown in nutrient broth culture and verified in the test systems listed earlier.

2) Individual isolates from the mud-water samples and from the mud-water mixtures in each test septum bottle were re-isolated after functioning as "pure" cultures in test septum bottles containing the organic solvents. These

procedures were carried out under aerobic and anaerobic conditions as outlined above because it was speculated that anaerobic bacteria may have been introduced with aerobic heterotrophs that had been knowingly inoculated into the bottles and these may have been active agents or cooperating agents in degradation. These anaerobes could have been carried in the aerobic colonies originally isolated from the mud sample, but were not observed because they had been incubated aerobically up until the time they were put into the full serum bottles. The reverse situation could have been true for aerobic or microaerophilic bacteria carried in anaerobic cultures. In order to detect mixed cultures, all cultures were examined by streaking duplicate R2-A plates with inoculum from each serum bottle. One set of plates was incubated aerobically; the other was incubated anaerobically in a BBL Gas Pac disposable system. All recognizably different colonies resulting from these treatments were subcultured to purify and subjected to identification procedures outlined earlier.

### C1731

1) The observation in the laboratory of the formation of lower molecular weight chlorinated organic compounds from common organic solvents supports our theory of their origin in raw water.

2) Finding the laboratory results duplicated in the Vero Beach spill further supports our theory.

## C18 Biodegradation of Tetrachloroethylene in Pure Cultures Using the Isolation Procedure Described Above (717)

What was thought to be seven pure cultures were isolated, and designated "Bacterial Isolates 1 through 7." These seven cultures were placed in sterilized culture media in sterilized sealed vials with approximately 200 μg of tetrachloroethylene. In addition, four common bacteria in pure culture were included in the test, as well as a mixed blend of all the anaerobic bacteria isolated from the Muck-Water Sample 1. Tetrachloroethylene was also added to sterilized culture media and distilled water as controls. These pure culture tests were designated Test 3.

### C181 Results of Test 3

Test 3 was begun on March 20, 1979 and the sealed vials were tested for chlorinated organics on March 31 and and April 7, after 10 and 17 days aging. The results are shown in Table 58. The tetrachloroethylene sample used in Test 3 was the same sample used in Test 2. Therefore, the approximate 200 g sample that was studied contained approximately 3.7 μg of trichloroethylene, a trace of trans and cis 1,2-dichloroethene, 0.32 μg of methylene chloride and/or vinylidene chloride and 0.1 μg of vinyl chloride

## TABLE 58

## BIODEGRADATION OF TETRACHLOROETHYLENE (APPROX. 150 µg) IN CULTURE MEDIA WITH SPECIFIC BACTERIA (TEST 3)

|  | µg of chlorinated compounds after aging |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | 10 days |  |  |  |  | 17 days |  |  |  |  |
| Bacteria | tetra | tri | cis | M.C. and/or viny. ch. | V.C. | tetra | tri | cis | M.C. and/or viny. ch. | V.C. |
| Bacterial Isolate 1 | 131 | 23 | 38 | 2.2 | ND | 115 | ND | 0.4 | 0.5 | ND |
| Bacterial Isolate 2 | 124 | 1.1 | 1.6 | 0.4 | ND | 108 | ND | 0.2 | 0.4 | ND |
| Bacterial Isolate 3 | 111 | 0.08 | 1.5 | 0.92 | ND | 74 | ND | ND | 0.8 | ND |
| Bacterial Isolate 4 | 93 | 7.2 | 8.2 | 1.0 | ND | 81 | ND | ND | 0.8 | ND |
| Bacterial Isolate 5 | 87 | nil | 0.2 | 0.7 | ND | 73 | ND | 0.6 | 0.6 | ND |
| Bacterial Isolate 6 | 96 | 17.4 | 20.1 | 2.5 | ND | 75 | ND | 0.14 | 1.07 | ND |
| Bacterial Isolate 7 | 86 | 0.2 | 0.2 | 0.8 | ND | 71 | ND | 0.1 | 0.7 | ND |
| *Proteus vulgaris* | 133 | ND | 0.4 | 0.8 | ND | 71 | ND | 0.4 | 0.3 | ND |
| *E. cloacae* | 130 | ND | 0.4 | 0.7 | 0.2 | 109 | 8.2 | ND | 2.1 | 0.2 |
| *E. coli* | 131 | ND | 0.2 | 0.9 | 0.3 | 92 | 8.2 | 27 | 1 | 0.3 |
| *P. aeruginosa* | 128 | ND | 0.2 | 1.03 | 0.3 | 117 | 5.7 | ND | 1.1 | 0.3 |
| Muck anaerobic mix | 92 | ND | 0.9 | 0.8 | ND | 83 | ND | 0.2 | 0.6 | ND |
| Sterilized culture control | 193 | 3.2 | ND | trace | trace | 187 | 2.9 | ND | ND | ND |
| Sterilized distilled water control | 189 | 3.0 | ND | trace | trace | 193 | 2.7 | ND | ND | ND |

After all the 10-day aged test vials were analyzed for chlorinated organics, approximately one-tenth mL from the contents of each vial was removed and examined bacteriologically. Results of these analyses are shown in Table 59.

As shown in Table 59, 4 of the 7 Bacterial Isolates were not pure, but contained two or three types of bacteria.

In the Bacterial Isolate 1 vial tested on day 17, (Table 58), it was observed that further reduction of tetrachloroethylene occurred, but the increased levels of chlorinated by-products seen on test day 10 had disappeared. After the 17-day analysis, we examined the vial contents bacteriologically. Results of these analyses are shown in Table 59. The bacterial composition of the Isolate vial 1 had changed. This observed change may indicate that conditions in the vial then favored the degradation of the chlorinated by-products.

Isolate 2 vial after 10 days aging, (Table 58), showed a decreased level of tetrachloroethylene and small increases in the levels of chlorinated by-products. After 17 days, further depletion of tetrachloroethylene was observed, with a concomitant reduction in by-products. In Table 59, the bacterial composition changed from day 10 to day 17. *Pseudomonas fluorescens* may have been introduced during sampling of the test vial on day 10.

Isolate 3 vial at 10 and 17 days, (Table 58), followed the pattern of Isolate 2 except tetrachloroethylene was found in lower levels. The bacterial composition, (Table 59), apparently did not change.

Isolate 4 vial at 10 and 17 days exhibited behavior similar to Isolate 1 vial except for greater decay of tetrachloroethylene and less increase in by-products. Once again, the bacterial composition (Table 59), did not change from day 10 to day 17.

Isolate 5 vial at 10 and 17 days showed depletion of tetrachloroethylene with small increases in by-products. Only *P. fluorescens* was found on day 10, (Table 59). Bacterial analyses were not made on day 17.

Isolate 6 vial at 10 and 17 days, exhibited behavior similar to Isolate 1 vial. The bacterial composition was not found to change (Table 59). Only *P. maltophilia* and *P. fluorescens* were found.

Isolate 7 vial behaved like Isolate 5 vial. Only unidentified, G-short, wide rods were present on test day 10, (Table 59) and bacterial analyses were not done on day 17.

The vials containing the four common bacteria, Table 58, all exhibited varying decreases of tetrachloroethylene concentrations after the 10-day test period, with some low level increase of chlorinated by-products. After day 17, the vial inoculated with *Proteus vulgaris* showed further decrease of tetrachloroethylene but no increase in by-products. Vials inoculated with *Enterobactor cloacae*, *Escherichia coli* and *P. aeruginosa* exhibited increased

# TABLE 59

## IDENTIFICATION OF SPECIFIC BACTERIA IN THE "BACTERIAL ISOLATES" IN TEST 3

| | March 31 after 10 days aging: | | April 7 after 17 days aging: | |
|---|---|---|---|---|
| | Specific bacteria found | Plating Growth Conditions | Specific bacteria found | Plating Growth Conditions |
| Bacterial Isolate 1 | G + cocci (tetrads)<br>*C. cadaveris*<br>*C. limosum* | aerobic & anaerobic<br>anaerobic<br>anaerobic | G + cocci (tetrads)<br>Big G + rods and filaments, (Trichome?) | aerobic & anaerobic<br>anaerobic |
| Bacterial Isolate 2 | *C. limosum* | anaerobic | Big G var. rods and filament<br>*P. fluorescens* | anaerobic |
| Bacterial Isolate 3 | *P. maltophilia*<br>Big G + rods | aerobic & anaerobic<br>aerobic & anaerobic | *P. Maltophilia*<br>Big G + rods | aerobic & anaerobic<br>aerobic & anaerobic |
| Bacterial Isolate 4 | *P. fluorescens*<br>*P. maltophilia* | aerobic & anaerobic<br>aerobic & anaerobic | *P. fluorescens*<br>*P. maltophilia* | aerobic & anaerobic<br>aerobic & anaerobic |
| Bacterial Isolate 6 | *P. fluorescens*<br>*P. Maltophilia* | aerobic & anaerobic<br>aerobic & anaerobic | *P. fluorescens*<br>*P. maltophilia* | aerobic & anaerobic<br>aerobic & anaerobic |
| Bacterial Isolate 5 | *P. fluorescens* | aerobic | not determined on this date | |
| Bacterial Isolate 7 | G - short, wide rods | aerobic & anaerobic | not determined on this date | |

levels of chlorinated by-products after day 17, including some vinyl chloride.

The vial containing the muck anaerobic mix (Table 58), showed tetrachloroethylene decay with minor increases in by-products growth at both 10 and 17 days. Bacterial analyses were made after test day 10. As shown in Table 59, large unidentified G+ rods were found.

The Sterilized Culture Control and Sterilized Distilled Water Control test vials, Table 58, showed no decay of tetrachloroethylene.

### C183 Graphic Plots of Test 3 Data

Graphic plots comparing the biodegradation rates by each test vial in Test 3 of tetrachloroethylene in culture media are shown in Figures 91 and 92. The biodegradation rate of tetrachloroethylene by muckwater Sample 1 (Test 2) is also shown. In Figure 91, all vials containing the seven Bacterial Isolates show more rapid depletion of tetrachloroethylene than the muck-water test vial. Some of the isolate test vials show much more rapid degradation than others. Similar conclusions can be drawn from Figure 92, for the test vials shown.

### C19 Biodegradation of tetrachloroethylene in other muck-water samples (Test 4)

At the end of Test 3, April 7, 1979, the original Everglades muckwater Sample 1, collected February, 1979, was depleted. From the end of April to the end of October, 1979, we collected five more muck-water samples and tested

TABLE 60

SAMPLE SITES OF MUCK AND WATER
USED IN BIODEGRADATION EXPERIMENTS (TEST 4)

| Muck-Water Sample | Location | |
|---|---|---|
| 2 | Tamiami Trail (U.S. 41) roadside ditch, 8 miles east of L-67 | Apr. 25, 1979 |
| 3 | L-67 (not same location as 1 -approx. 4 miles N. | May 10, 1979 |
| 4 | L-67 one-half mile south of 5 | Aug. 15, 1979 |
| 5 | L-67 same areas as muck-water Sample 1 | Aug. 15, 1979 |
| 6 | L-67 one-half mile north of 5 | Aug. 15, 1979 |
| 7 | L-111 one-quarter mile west of U.S. 1 | Dec. 3, 1979 |

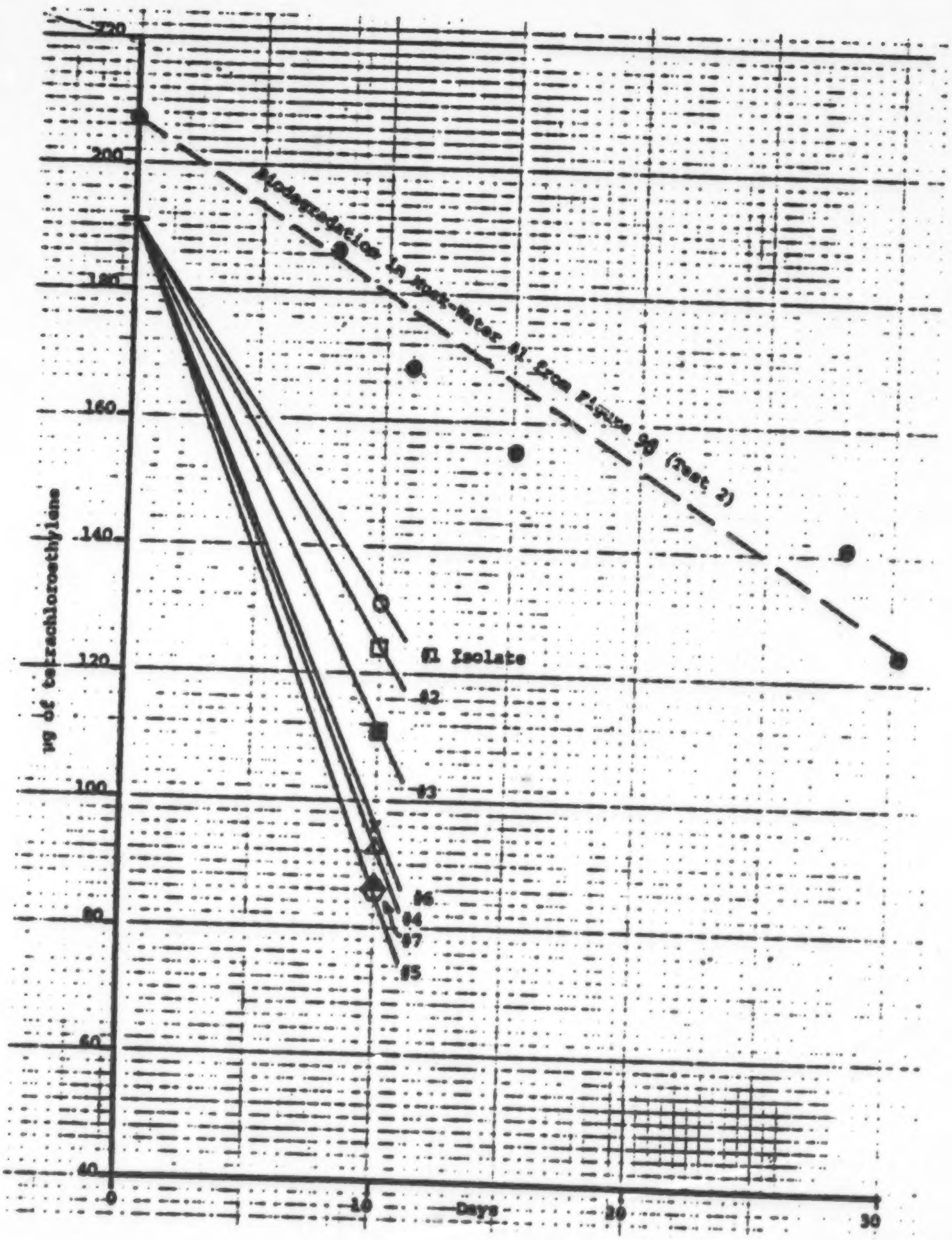


Figure 91 Biodegradation of tetrachloroethylene in culture media with specific bacteria isolated from Everglades Muck Sample #1. (Test 3)

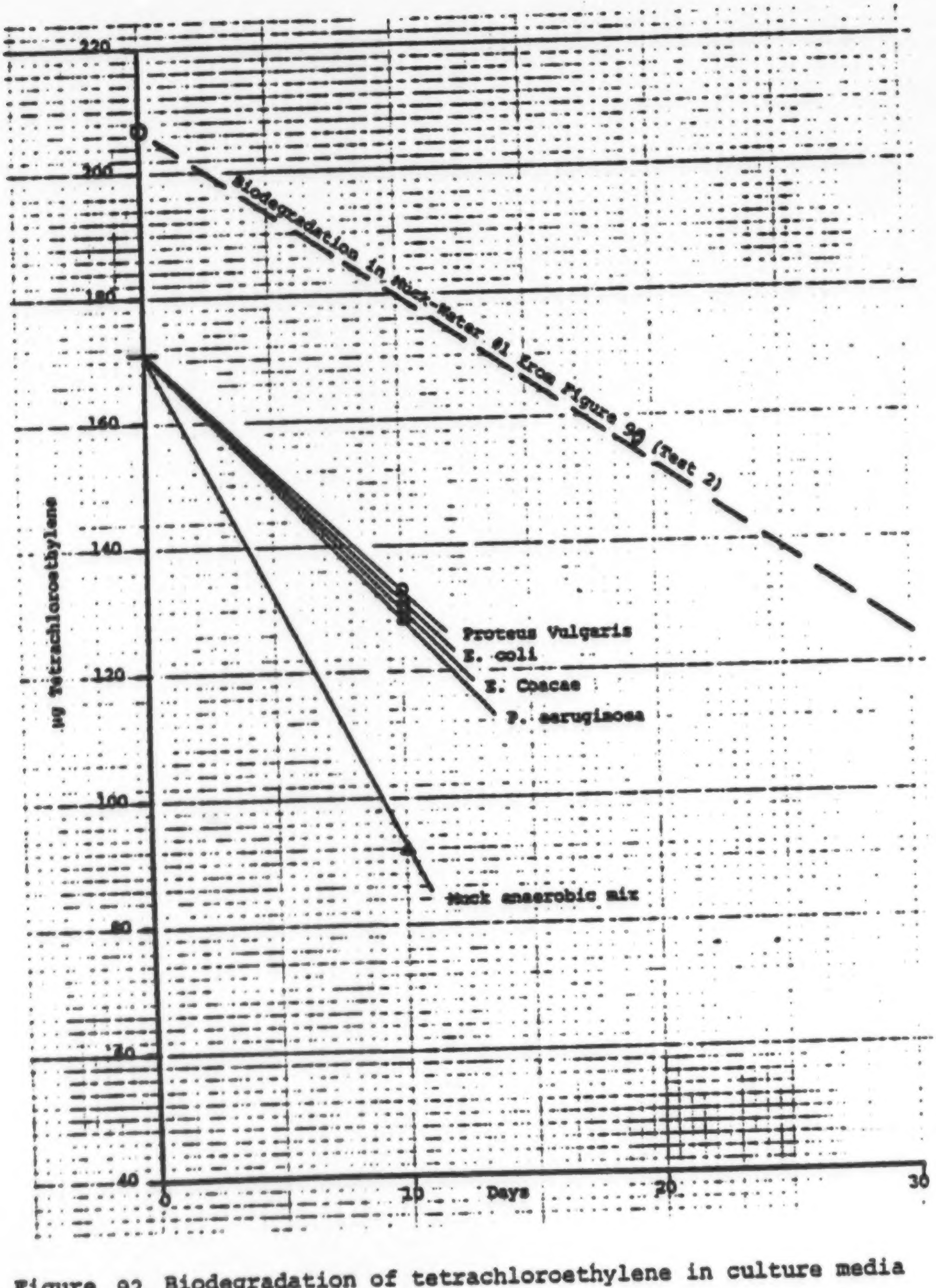


Figure 92 Biodegradation of tetrachloroethylene in culture media with four common bacteria and a mixture of anaerobic bacteria from Muck. (Test 3)

their ability to biodegrade tetrachloroethylene. We varied the level of tetrachloroethylene added to the vial experiments. The locations from which the samples were collected is shown in Table 60.

### C191 Results of Test 4

All five muck-water Samples 2 through 6, collected from the latter part of April to the end of October, caused depletion of tetrachloroethylene, but with only transient trace levels of chlorinated by-products. Sample 7, Table 60, was a Marl-Water Sample and it provided support for the evidence of product degradation that we found with Muck-Water 1.

The tetrachloroethylene biodecay rates for Samples 2 through 7 are shown in Figure 93. Once again, the rate of degradation in muck-water Sample 1 was included for comparison. All six samples, 2 through 7, showed similar tetrachloroethylene biodecay rates.

Marl-Water Sample 7 collected on December 3, 1979, in addition to exhibiting biodegradation of tetrachloroethylene, resulted in increases in concentration of some chlorinated by-products. These data are shown in Table 61. Contaminants present in the injected tetrachloroethylene are also shown. A decrease in tetrachloroethylene and an increase in trichloroethylene, cis-1,2-dichloroethylene and methylene chloride (and/or vinylidene chloride).

**TABLE 61**

**BIODEGRADATION OF TETRACHLOROETHYLENE**
**BY MARL-WATER SAMPLE 7 - TEST 4**
**(Approx. 250 g of tetrachloroethylene added to vial)**

(µg of chlorinated organics after 11 days of aging)

| | tetrachloro ethylene | trichloro-ethylene | cis-1,2-di-chloro-ethene | trans 1,2-di-chloro-ethene | methylene chloride and/or vinylidene chloride | vinyl chloride |
|---|---|---|---|---|---|---|
| tetrachloro-ethylene | 250 | 4.0 | tr | tr | 0.325 | 0.175 |
| Marl-Water Sample 7 | 212 | 4.7 | 2.3 | 0.07 | 1.2 | 0.06 |

No bacterial analyses were made of the sample and it was tested for chlorinated organics only after 11 days of aging.

### C110 Field Confirmation of Our Laboratory Biodegradation Work

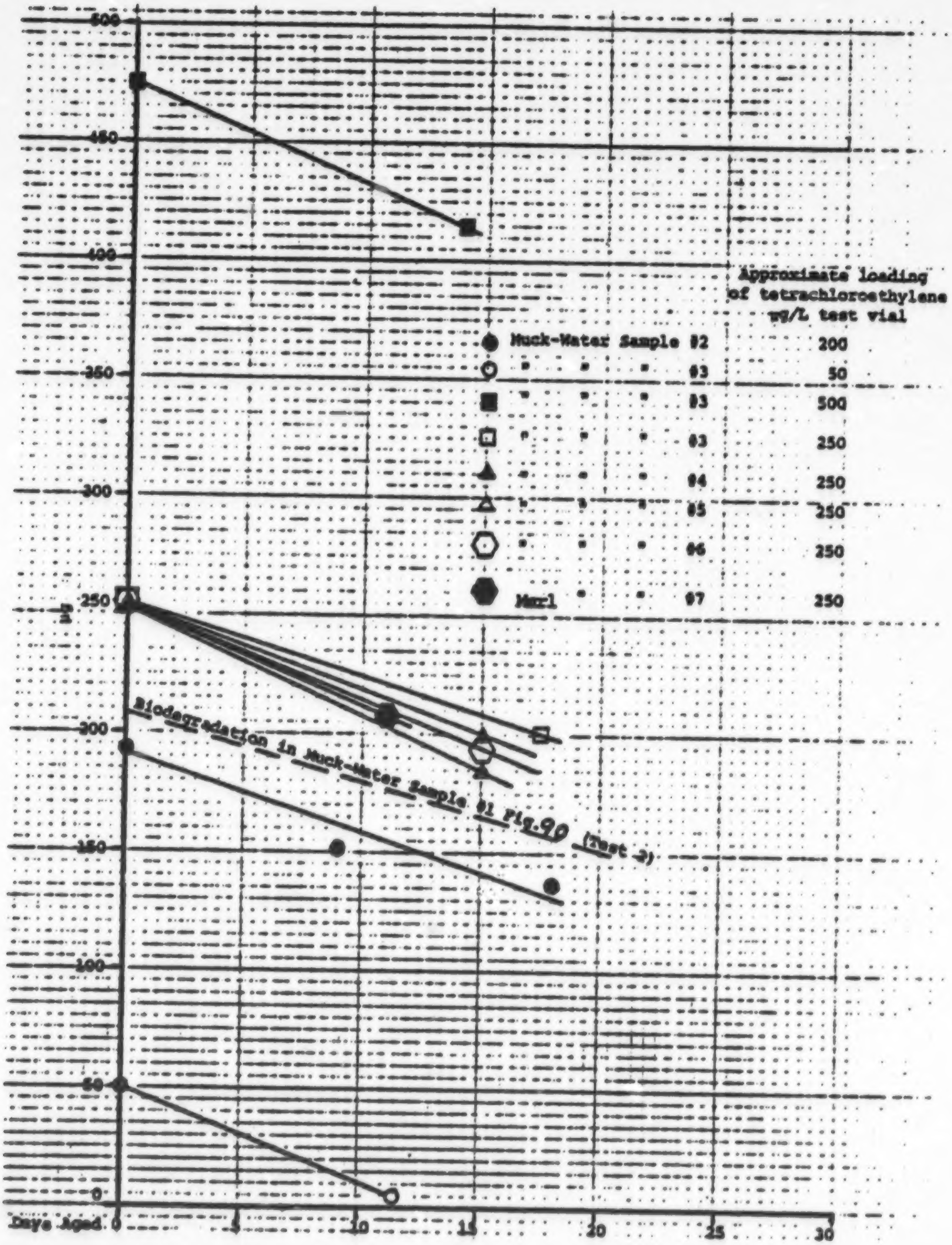


Figure 93 Biodegradation tetrachloroethylene with other Muck-Water Samples.

In March and April, 1980, water samples from the City of Vero Beach, Florida were analyzed. In Table 49 the 1978 analysis of finished water from the Vero Beach treatment plant compared to the output in April, 1980 is shown. The high level of a family of chloroethenes present in 1978 was the result of leakage from the underground storage tank of trichloroethylene used for metal cleaning at a small airport in Vero Beach. A municipal supply well was only 900 ft. away from the spill site. When trichloroethylene was found in Vero Beach water, this proximal well was closed, resulting in the analysis of finished water shown in Table 49 in April, 1980. Only low levels of the chlorinated biodegradation by-products of trichloroethylene were still present. In Reference 1, we show that these levels of substances are not formed from the chlorination of naturally occurring precursor substances present in all raw water.

In March, 1980, two samples of raw water from the contaminated well that had been taken out of service in Vero Beach were analyzed. The analysis is shown in Table 62.

### TABLE 62

### ANALYSIS OF WATER FROM CONTAMINATED WELL AT VERO BEACH, FLORIDA

µg/l

| | Trichloroethylene | Cis 1,2-Di chloroethene | Trans 1,2-Dichloroethene | Vinylidene chloride | Methylene chloride | Vinyl chloride |
|---|---|---|---|---|---|---|
| 3/11/80 | 374 | 1380 | 2.4 | 41.2 | 0.8 | 58.4 |
| 3/25/80 | 444 | 804 | 7.3 | 20 | 0.5 | 87.3 |

Both samples, March 11 and March 25, show that much of the originally spilled trichloroethylene had degraded to the lower molecular weight members of the chloroethene family of compounds and a small amount of methylene chloride. The ratio of chlorinated by-products is similar to the ratio obtained in laboratory biodegradation studies; i.e., the main product is cis-1,2-dichloroethene, followed by a small amount of trans-1,2-dichloroethene. The level of vinylidene is lower than the level of vinyl chloride. Only a small amount of methylene chloride was found, consistent with its high rate of biodegradation. All the chlorinated organics represented in Table 62, were confirmed by GC/MS. In this set of analyses we separated the two compounds, which in most of our work we classified as methylene chloride and/or vinylidene chloride. Most of the GC peak was due to vinylidene chloride with only a small amount of methylene chloride. We assume that this ratio applies to our study of the biodegradation of chloroethenes. When we studied biodegradation of chloromethanes and chloroethanes, we probably were measuring methylene chloride.

When we analyzed the well water sample collected on March 25, 1980, we also collected and analyzed a sample of the commercial grade trichloroethylene from the storage tank at the airport. A sample of 100 µg contained no detectable cis- or trans-1,2-dichloroethene, 0.13 g of methylene chloride and/or vinylidene chloride and 0.07 µg of vinyl chloride, which is typical of commercial grade trichloroethylene. The initial trichloroethylene leak at the airport occurred underground eliminating the possibility of U.V. degradation as a source of the chloroethene decay products formed. There was no trace of cis- or trans-1,2-dichloroethene in the spilled compound and only minor amounts of other by-products. We found that hydrolysis at ambient temperature does not give these results. The ratio of chlorinated by-products occuring several years after the airport spill indicates biodegradation as the cause. As this biodegradation occurred below ground level, it was probably anaerobic.

### C111 Biodegradation of Naturally Occuring Organics in Water

The observation of large numbers of a variety of heterotrophic bacteria in water and organic sediment taken from the Everglades west of Miami, Florida lead to the experiment to determine their effect on the natural organic solutes in water. The thought behind this being that if the sediment were removed as a source of replenishment of the organic solute load in the water, the indigenous bacteria would metabolize and decrease these organics.

We collected five gallons of clear water without organic sediment and kept it open to the atmosphere in the laboratory. Total organic carbon (TOC) in the water was determined on the day of collection (23 ppm) and for 11 days following, at which time the TOC had decreased to below detection limits. We have tried to repeat this experiment, but as summer advanced the sediment in the Everglades became more flocculant and was collected with the water thus precluding diminution of dissolved organic matter in a reasonable length of time. The water was not filtered as it was early demonstrated that the bacteria present were primarily associated with the suspended solids. We should like to repeat a refined version of the experiment and add air and limited nutrients to the surface water with a view to decreasing TOC, and thus THMFP, in drinking water source water. Precedent for this has recently been reported at the American Society for Microbiology meeting in May 1980 by Jamison (Ref. 37), who has had success removing man-made pollutants from ground water by controlling ground water flow (and thus pollutant spill migration) through the use of producer wells, developing effective native bacterial populations through nutrient supply wells, and recycling the entire water volume until the pollutant was reduced.

### C112 Conclusions on ED 3

1) Results of this study indicate that the source of the highly volatile chloroethene compounds, vinyl chloride, vinylidene chloride, cis- and trans-1,2-dichloroethene in our raw ground water is a result of biodegradation of trichloroethylene and/or tetrachloroethylene, which are found widely spread in the environment as a result of our use of these compounds.

2) Bacteria were isolated and identified from sediments and ground water. These were common soil bacteria and are sometimes present in municipal supply wells. Data are insufficient to conclude that these specific organisms caused the observed chemical changes. However, the chemical changes occurred in vials where living bacteria were detected and did not occur in vials that had been sterilized, which indicates that the chemical changes were caused by biological activity. Differences in the population composition among the vials, indicated by the different bacteria isolated from them, suggest that conditions within the vials were different. These undetermined condition differences (biotic and environmental) between vials may have been responsible for the differences in chemical results seen from vial to vial.

3) A simple laboratory method was developed for assaying biodegradation of highly volatile chlorinated organic compounds in water, soils and sediments, and bacteria culture media.

4) Almost all of the chlorinated methane, ethane, and ethene compounds were studied, and found to be susceptible to biodegradation.

5) The rate of biodegradation was determined for each compound. The bacterial population composition probably affects the kinds of intermediate biodegraded chlorinated organic compounds that are formed.

6) Certain bacterial populations and environmental conditions for example, may reduce all the tetrachloroethylene present in a given time, with the formation of only intermittent trace quantitites of lower chlorinated compounds.

7) Other bacterial populations and environmental conditions may reduce tetrachloroethylene with the formation of all possible lower chlorinated compounds.

8) The resulting concentration of the lower chlorinated compounds is dependent on the individual half life of each product and the favored end product of biodegradation in a given system. For example, biodegradation of tri- and/or tetrachloroethylene favors the production of cis- over trans-1,2-dichloroethylene by a factor of approximately 100:1. Therefore, while the biodegradation half life of the two compounds (cis and trans), is long and perhaps equal, the concentration of cis will always be much greater than trans.

9) Knowing the biodegradation half lives for the families of chlorinated compounds studied, we can understand and predict the chlorinated organic profile file of an environmental system after introduction of any single member of the families.

10) The results of analyses of water from a well near a below-ground spill of trichloroethylene support the results of our laboratory biodegradation study.

11) The bacterial population composition changes seasonally in the aquifer recharge basin as flooding and drydown occur in Florida. The underground

aquifer conditions may be more stable and support bacteria that favor production of the long-lived intermediate chlorinated compounds. However, it is still unknown where in the environment biodegradation occurs.

# LITERATURE CITED

1. Wood, P.R., D.F. Jackson, J.A. Gervers, D.H. Waddell and L. Kaplan (Project Officer, J. DeMarco). "Removing Potential Organic Carcinogens and Precursors from Drinking Water". Volume 1 and Appendix A (392 pages) MERL 760. EPA-600/2-80-130a.

2. Wood, P.R., J. DeMarco. "Effectiveness of Various Adsorbents in Removing Organic Compounds from Water. Part I - Removing Purgeable Halogenated Organics". USEPA Publication DWRD0008, Cincinnati, Ohio, September 1978.

3. Wood, P.R. J. DeMarco. "Effectiveness of Various Adsorbents in Removing Organic Compounds from Water. Part II - Removing Total Organic Carbon and Trihalomethane Precursor Substances". USEPA Publication DWRD009, Cincinnati, Ohio, September 1978.

4. Wood, P.R., J. DeMarco. "Effectiveness of Various Adsorbents in Removing Organic Compounds from Water - Removing Purgeable Halogenated Organics: (Chapter 4) Activated Carbon Adsorption of Organics from the Aqueous Phase, Volume 2, edited by J.J. McGuire and I.H. Suffet, Ann Arbor Science Publishers, Inc., Ann Arbor, MI ©1980.

5. Wood, P.R., J. DeMarco. "Removing Total Organic Carbon and Trihalomethane Precursor Substances". (Chapter 5) Activated Carbon Adsorption of Organics from the Aqueous Phase, Volume 2, edited by M.J. McGuire and I.H. Suffet, Ann Arbor Science Publishers, Inc., Ann Arbor, MI ©1980.

6. Wood, P.R., J. DeMarco. "Treatment of Groundwater with Granular Activated Carbon". Journal AWWA, November 1979. Part I, pp 674-682.

7. Glaze, W.H., et. al. "Evaluation of Biological Activated Carbon for Removal of Trihalomethane Precursors". Final Report on Contract No. CR-806157 to J. Keith Carswell, project officer, Drinking Water Research Division, MERL, Cincinnati, Ohio 45268, December 1982.

8. Rice, R.G., C.M. Robson and G.W. Miller, "An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies". EPA-600/2-78-147, U.S. Environmental Protection Agency, Cincinnati, Ohio 1978.

9. Rice, R.G., C.M. Robson, G.W. Miller, J.C. Clark and W. Kuhn, "Biological Processes in the Treatment of Municipal Water Supplies", EPA-600/2-80-1980, U.S. Environmental Protection Agency, Cincinnati, Ohio 1980.

10. APHA, AWWA, WPCF. 1975. Standard Methods for the Examination of Water and Wastewater. 14th Ed., APHA, Washington, D.C., p1139.

11. Reasoner, D.J., and E.E. Geldreich. 1979. A New Medium for Enumeration and Subculture of Bacteria from Potable Water. Abst. #N7, Annual Meeting ASM, p180, Los Angeles, CA.

12. Van der Kooij, D. 1976. Some Investigations into the Presence and Behavior of Bacteria in Activated Carbon Filters. In: Sontheimer, H., Ed. Translations of Reports on Special Problems of Water Technology, Vol. 9, EPA Report, EPA 600/9--76-030, 348-354.

13. Loewy, A.G., and P. Siekevitz. 1969. *Cell Structure and Function*. Holt, Rinehart, and Winston, New York, 516pp.

14. Klotz, M., P. Werner, and R. Schweisfurth. 1976. Investigations concerning the Microbiology of Activated Carbon Filters. In: Sontheimer, H., Ed. Translations of Reports on Special Problems of Water Technology, Vol. 9, EPA Report, EPA 600/9-76-030.

15. Cairo, P.R., J. McElhaney and I.H. Suffet. 1979. Pilot Plant Testing of Activated Carbon Adsorption Systems. *Jour. AWWA*, 71:660-673.

16. Schalekamp, M. 1979. The use of GAC Titration to Ensure Quality in Drinking Water from Surface Sources. *Jour. AWWA*, 71:638-647.

17. Symons, J.M., J.K. Carswell, J. DeMarco and O.T. Love, Jr. "Removal of Organic Contaminants from Drinking Water Using Techniques other than Granular Activated Carbon Alone" (A Progress Report). Drinking Water Research Div., Municipal Environ. Res. Laboratory, Office of R&D, US-EPA, Cincinnati, Oh 45268, May 1979, 60pp.

18. Liss, P.S., and P.G. Slater. "Flux of Gases Across the Air-sea Interface". Nature, Vol. 247, January 25, 1974, pp 181-184.

19. Mackay, D., and P.J. Leinonen. "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere". Environmental Science and Technology, Vol. 9, No. 13, December 1975. pp 1178-1180.

20. Cohen, Y., W. Cocchio, and D. Mackay. "Laboratory Study of Liquid-phase Controlled Volatilization Rates in Presence of Wind Waves". Environmental Science and Technology, Vol. 12, No. 5, May 1978. pp 553-558.

21. Mackay, D., W.Y. Shiu, and R.P. Sutherland. "Determination of Air-water Henry's Law Constants for Hydrophobic Pollutants". Environmental Science and Technology, Vol. 13, Mar. 1979. pp 333-337.

22. Dilling, W.L., N.B. Tefertiller, and G.J. Kallos. "Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-trichloroethane, Trichloroethylene, Tetrachloroethylene, and other Chlorinated Compounds in Dilute Aqueous Solutions". Ibid. Vol. 9, Sept. 1975. pp 834-837.

23. Dilling, W.L., "Interphase Transfer Processes. II. Evaporation Rates of Chloromethanes, Ethanes, Ethylenes, Propanes, and Propylenes from Dilute Aqueous Solutions. Comparisons with theoretical predications.

24. McCarty, P.L., D.G. Argo, J. English, et. al., "Water Factory 21: Inorganic, Organic, and Biological Quality of Reclaimed Wastewater and Plant Performance". Technical Report No. 226, January 1978. Department of Civil Engineering, Stanford University.

25. Mackay, D., and A.W. Wolkoff. "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere". Environmental Science and Technology.

26. Beeman, C.P., R.F. Lang and D.F. Jackson. "Survey of Trihalomethane Distribution in Various Potable Water Supply Sources in the State of Florida". Prepared for the Bureau of Drinking Water and Special Programs, Florida Department of Environmental Regulation, Tallahassee, FL, by Florida International University, Miami, FL, June 1978.

27. Dilling, W.L., C.J. Bredeweg and N.B. Tefertiller. "Organic Photo chemistry Simulated Atmospheric Photodecomposition Rates of Methylene Chloride, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene and Other Compounds". Environmental Science and Technology, 10(4):351-357, April 1976.

28. Alexander, M. "Microbial Metabolism of Chemicals of Environmental Concern". ASM News, 46(1):35-38, 1980.

29. Barth, E.F., R.L. Bunch. "Biodegradation and Treatability of Specific Pollutants". EPA-600-9-79-034, Municipal Environmental Research Laboratory, Office of Research and Development, US-EPA, Cincinnati, OH 45268, Oct. 1979.

30. National Academy of Sciences, Washington, D.C. "Chloroform, Carbon Tetrachloride, and Other Halomethanes: An Environmental Assessment". 1978.

31. McConnell, G., D.M. Ferguson and C.R. Pearson. "Chlorinated Hydrocarbons and the Environment". Endeavour 34:13-18, 1975.

32. Cox, R.A., R.G. Derwent, A.E.J. Eggleton, and J.E. Lovelock. "Photochemical Oxidation of Halocarbons in the Troposphere". Atmospheric Environment 10(4):305-308, 1976.

33. Rittman, B.E., and P.L. McCarty. "Utilization of Dichloromethane by Suspended and Fixed-Film Bacteria". Applied and Environmental Microbiology, 39(6):1225-1226, June 1980.

34. McCarty, P.L., K.H. Sutherland, J. Graydon, and M. Reinhard. "Volatile Organic Contaminants Removal by Air Stripping". A report by Environmental Engineering and Sciences, Civil Engineering Department, Stanford University, Stanford, CA.

35. Bellar, T.A. and J.D. Lichtenberg. "Determining Volatile Organics and Microgram per Liter Levels in Water by Gas Chromatography". JAWWA, 66(12)739-744 (1974).

36. Dressman, R.C., and E.F. McFarren. "Sample Bottle Purging Method for Determination of Vinyl Chloride in Water at Submicrogram Per Liter Levels". J. of Chrom. Science, Vol. 15, Fed. 19, 1977, pp 69-72.

37. Jamison, V.W. and R.L. Raymond. Microbiological clean up of contaminated ground water. Paper presented at the 1980 Annual Meeting of the American Society for Microbiology, Miami Beach, FL, May 11-16, 1980.

38. Hoigne, J. and Bader, H., "Ozonation of Water: Selectivety and Rate of Oxidation of Solutes", Ozone: Science and Engineering, Vol. 1, pp 73-75, 1979.

39. Rice, R.G., et. al. "Ozone for Industrial Water and Wastewater Treatment". EPA-600/2-80-060, April 1980.

40. Umphres, M.D., et. al. "Trihalomethanes in Drinking Water". Water Engineering and Management, April 30, 1981. Page R-65 to R-74.

41. Miller, G.W., et. al., "An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies". EPA-600/8-78-018, Oct. 1978.

42. Grob, K. and Zurcher, F. "Stripping of Trace Organic Substances from Water Equipment and Procedure". Jour. Chromatogr., 117:285 (1976).

43. McQuire, M.J., Krasner, S.W., Hwang, C.J. and Izaguirre, G. "Close-Loop Stripping Analysis at the Parts-Per-Trillion Level as a Tool for Solving Taste and Odor Problems". AWWA Technology Conference Proceedings, Advances in Laboratory Techniques in Quality Control, Dec. 1980.